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GEOLOGICAL SURVEY OF OHIO

EDWARD ORTON, Jr., State Geologist.

FOURTH SERIES, BULLETIN No. 3.

THE MANUFACTURE OF HYDRAULIC CEMENTS

BY

ALBERT VICTOR BLEININGER, B. Sc.

Instructor in Ceramics, Ohio State University.

Published by authority of the Legislature of Ohio, under the Supervision of the State Geologist.

COLUMBUS, OHIO, DECEMBER, 1904.

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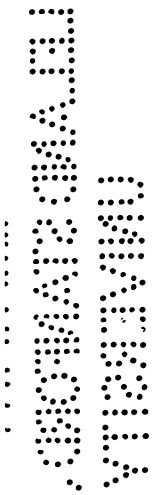

LETTER OF TRANSMITTAL.

To His Excellency, MYRON T. HERRICK, *Governor of Ohio:*

SIR:—I have the honor to present to you, herewith, the Third Bulletin of the Geological Survey, which has been prepared under my supervision. The subject of the report is the Manufacture of Hydraulic Cements, and its preparation has been under the personal charge of Mr. Albert Victor Bleininger, B. Sc., of the Ohio State University. It represents almost four years of unflagging and enthusiastic labor and I believe it is a contribution to knowledge, the importance of which will be promptly recognized.

I have the honor to be

Yours very respectfully,

EDWARD ORTON, JR., E. M.

State Geologist.

Ohio State University,
December, 1904.

78752

OFFICERS OF THE SURVEY.

EDWARD ORTON, JR., E. M. ..... State Geologist
Economic Work in Cement and Clay Industries.

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Technological Work in Cement Manufacture.

SAMUEL VERNON PEPPEL, B. Sc. ..... Special Assistant
Technological Work in Lime and Sand Brick Industries.

METTA L. SEYMOUR ..... Stenographer and Clerk

ANNOUNCEMENTS BY THE STATE GEOLOGIST.

BULLETIN 3.

The following Bulletin deals with the manufacture of hydraulic cements, a subject upon which little reliable information has been spread abroad. That which has been published has been in large portion in other languages than English.

The marvelous expansion in recent years in hydraulic cement manufacture and the Portland cement industry, in particular, has resulted in a condition which is undesirable in several respects. Accurate information as to the nature of the raw materials best suited has not been available and hence industries have been established at sites which are now known to be unfavorable, and where the local supplies must be rejected and others transported at a great permanent disadvantage if the output reaches a grade where its use is safe and proper. Also, chemists whose training has been so directed as to give them facility in the class of problems here met are exceedingly scarce, and thus many plants have gotten into the way of running along with only the baldest daily essentials from the laboratory instead of asking and receiving from the chemist that class of information and advice which would enable them to rapidly conquer the obstacles and smooth away the difficulties which every new cement industry must inevitably face. Also, managers and directors of cement industries, not being able to obtain in any place a succinct statement of what has been done in this field of research, have sometimes adopted mistaken and dangerous policies as to their product, because the defects arising are mostly slow to develop and obscure, and have thus placed upon the market thousands of barrels of poor material whose use tends to discredit cements as a class, and prevent the superlative usefulness of good cements from being earlier and more fully recognized.

It has been my intent and desire in authorizing and supervising the preparation of this volume to place within the reach of every intelligent person who desires it, a statement of what materials are needed to make good cements, of what mechanical treatment is necessary, and what effects will result from deviations from the prescribed quality of materials or treatment. It is not possible to convey these ideas without constant use of chemical nomenclature and chemical conceptions.

It may be that the book will be a disappointment on this account to some persons who are interested in the industry, but who have not the

training to readily grasp chemical conceptions. It has been written under the belief that the cement industry is really a branch of chemical engineering and that no one devoid of chemical and engineering training can be safely placed in control or high in the councils of this industry. To cement chemists, and managers of plants, the work will doubtless be readily accessible and it is hoped that the practical conclusions reached in all parts of the book will be available to all interested persons, whether the reasoning and investigations by which the conclusions are reached are equally clear or not.

I wish to record at this place my high appreciation of the work which Mr. Bleininger has put upon this volume. His search of the literature has been as thorough as his opportunities have afforded; his own laboratory researches have been most painstaking and laborious, and as a rule have been done by his own hands, in the intervals of his daily busy routine. His acquaintance with the various plants of the country is by no means confined to Ohio, as he covered the country in the course of his studies. He has pursued this work at financial sacrifices to himself, which is the best evidence of his genuine scientific devotion to his work.

It is with a knowledge of these things that I take pleasure in commending the volume to the public.

FORMER PUBLICATIONS OF THE SURVEY.

The work performed by the First, Second and Third organizations of the Geological Survey of Ohio is comprehended in the following list of publications:

FIRST GEOLOGICAL SURVEY 1837-1838.

Title of Volume.	Date of Issue.	Number of Pages.	Number of Copies Printed.	Geologist in Charge.
First Annual Report.....	1838	134	5,000	W. W. Mather
Second Annual Report.....	1838	236	5,000	W. W. Mather

SECOND GEOLOGICAL SURVEY 1869-1888.

Title of Volume.	Date of Issue.	Number of Pages.	Number of Copies Printed.	Geologist in Charge.
Report of Progress.....	1869	176	14,500	J. S. Newberry
Report of Progress.....	1870	568	14,500	J. S. Newberry
Report of Progress.....	1871	3	400	J. S. Newberry
Geology of Ohio, vol. I, part I, Geology.....	1872	680	20,000	J. S. Newberry
Geology of Ohio, vol. I, part II, Paleontology.....	1873	*401 †49	20,000	J. S. Newberry
Geology of Ohio, vol. II, part I, Geology.....	1874	701	20,000	J. S. Newberry
Geology of Ohio, vol. II, part II, Paleontology.....	1875	*431 †59	20,000	J. S. Newberry
Geology of Ohio, vol. III, Geology.....	1878	958	20,000	J. S. Newberry
Geological Atlas of Ohio.....	1879		5,000	J. S. Newberry
Geology of Ohio, vol. IV, Zoology and Botany.....	1882	1,070	20,000	J. S. Newberry
Geology of Ohio, vol. V, Economic Geology.....	1884	1,124	10,000	Edward Orton
Preliminary Report on Petroleum and Inflammable Gas..	1886	76	2,500	Edward Orton
Geology of Ohio, vol. VI, Economic Geology.....	1888	831	15,000	Edward Orton

*Pages. †Plates.

THIRD GEOLOGICAL SURVEY 1889-1864.

Title of Volume.	Date of Issue.	Number of Pages.	Number of Copies Printed.	Geologist in Charge.
First Annual Report.....	1890	323	10,000	Edward Orton
Geology of Ohio, vol. VII, part I, Economic Geology..	1893	290	2,500	Edward Orton
Geology of Ohio, vol. VII, (complete including part I)..	1894	970	7,500	Edward Orton

1—S. G. Bull.

FOURTH GEOLOGICAL SURVEY 1889———.

Title of Volume.	Date of Issue.	Number of Pages.	Number of Copies Printed.	Geologist in Charge.
Bulletin 1	1903	320	8,000	Edward Orton, Jr.
Bulletin 2	1904	260	6,000	Edward Orton, Jr.

DISTRIBUTION OF REPORTS.

First Geological Survey.—These volumes are out of print and rare. They can only be procured from dealers in second-hand libraries and are difficult to obtain even there.

Second Geological Survey.—These volumes were all distributed at the time of their issue. The State retained no stock for meeting future demands, so that no copies of any of these volumes can be obtained from the office of the State Geologist. They can be bought in many second-hand book stores and from dealers in old libraries, at prices varying from a few cents to two or three dollars per volume, according to rarity and demand. Volumes V and VI are the rarest and most sought for.

Third Geological Survey.—These volumes were all distributed at the time of issue, except Volume VII. of which 1,500 were put in the hands of the Secretary of State, for sale at cost of publication. Of these, a few remain at the date of the publication of this volume. The price is $1.50. To obtain copies, send postal or money order to the Secretary of State, State House, Columbus, Ohio. No other volume can be obtained from this source .

The other volumes of this series can be procured only from second-hand book and library dealers.

Fourth Geological Survey.—Under the law, copies of these Bulletins can be bought at the office of the State Geologist, at the cost of publication. Postal orders, money orders, checks, drafts, or currency must accompany orders. Stamps will not be received.

Bulletin 1—Oil and Gas..... $0.65
Bulletin 2—Use of Cement $0.30
Bulletin 3—Manufacture of Cement.....
Bulletin 4—Lime Industry of Ohio.....In preparation
Bulletin 5—Lime-Sand Brick Industry.....In preparation
Bulletin 6—Salt Industry of Ohio.....In preparation

THE LAWS UNDER WHICH THE SURVEY OPERATES.

For the information of the public, the law under which the work of the Survey is prosecuted is herewith published:—

Laws of Ohio, 1889, vol. 86, p. 262.

(Senate Bill 409.)

AN ACT

To provide for the extension of the Geological Survey of the State.

Section 1. Be it enacted by the General Assembly of the State of Ohio, That the governor is hereby authorized to appoint a state geologist, whose duty it shall be to continue and extend the investigations already made into the geological structure and resources of the state. Said state geologist shall be appointed for a term of three years, but he may be removed for cause at any time, and a successor appointed in his stead; and the governor is authorized to fill any vacancy which may occur from any cause, at any time. The compensation of said state geologist shall be at the rate of two hundred dollars per month, for the time actually employed; and said geologist shall have power to employ such assistants as he may need; but in no event shall the salary of the geologist, pay to assistants, and expense of the department, exceed the amount of the expenditure authorized by the general assembly.

Section 2. It shall be the duty of said geologist to study, and determine as nearly as possible, the number and extent of the various formations of the state; to represent the same, from time to time, upon properly constructed maps and diagrams; to study the modes of occurrence and the distribution of the useful minerals and products of these formations; to determine the chemical composition and structure of the same; to investigate the soils and water supply of the state; and to give attention to the discoveries of coal, building stone, natural cement, petroleum, gas and other natural substances of use and value to the state. He may also collect and describe the fossils of the various geological formations of the state; but no expenditure shall be incurred under this head that is not expressly ordered and provided for by the general assembly.

Section 3. The said geologist shall make, on or before the first day in February of each year, a report to the governor, covering the work of the preceding year, and the report shall be transmitted to the general assembly, to be printed in the same manner as other public documents, or as shall be otherwise ordered.

Section 4. The salaries of the state geologist, and the assistants employed by him, together with the traveling and incidental expenses, shall be paid monthly, on presentation of properly itemized vouchers, signed by the governor, out of the state treasury, from the appropriation made for such purpose.

Section 5. There is hereby appropriated from the general revenue fund the sum of one thousand dollars annually, for the purpose above named.

Section 6. This act shall take effect and be in force from and after its passage.

NOAH H. ALBAUGH,
Speaker pro tem. of the House of Representatives.
THEODORE F. DAVIS,
Passed April 12, 1889. President pro tem. of the Senate.

The powers and duties of the State Geologist under this act were made so broad and general as to permit carrying on almost any work, so that no new legal provision was thought necessary in connection with re-opening the work of the survey under the Fourth organization. The sum designated in Section 5 is not made a limiting condition of the law, so that the Legislature may appropriate any other amount, at is discretion,

for carrying on the work. Acting under the law, the Legislature has made the following appropriations for geological work.

Designation of Legislature.	Year.	Amount Appropriated.
Seventy-Fourth	1900	$2,500 00
Seventy-Fourth	1901	$3,500 00
Seventy-Fifth	1902	$5,000 00
Seventy-Fifth	1903	$3,000 00
Seventy-Sixth	1904	$2,800 00
Seventy-Sixth	1905	$2,900 00

LAW OF 1902 ON PUBLICATION.

The law providing for the publication and distribution of reports is as follows:

Laws of Ohio, 1902, vol. 95, p. 593.

(House Bill, 800).

AN ACT

To Provide for the Publication and Distribution of the Reports of the State Geologist.

Section 1. Be it enacted by the General Assembly of the state of Ohio, that whenever the state geologist shall have completed a bulletin upon any of the subjects upon which he is authorized to conduct investigations, he shall notify the State Printing Commission of this fact, and it shall be the duty of this Commission to determine the number of copies which shall be printed, and the grade of paper, the kind of binding, and any other details incident to its proper publication.

Section 2. It shall be the duty of said Commission to provide for the publication of said bulletin as soon as possible after the completion of the same. The issue shall consist of a minimum number of three thousand copies.

Of these, one thousand copies, after deducting 200 for the state library, shall be distributed pro rata among the general assembly.

One thousand shall be distributed free by the state geologist in exchange with other surveys, and with individuals whose services have been used in the collection or preparation of the matter for the bulletins. Of this number not more than four hundred may be distributed during the first year after publication, and not more than fifty in any subsequent year.

One thousand copies shall be set aside for binding along with other bulletins from time to time. When a sufficient number of such bulletins have accumulated to make collectively a volume of from 800 to 1,000 pages, they shall be bound, lettered and numbered, to take their place in the series of volumes already published by the survey.

The distribution of the bound volume of the survey shall be in the hands of the state geologist; but the state library shall receive ten copies, each member of the general assembly one copy, with privilege to draw not to exceed two other copies on application, and public libraries in the state shall be supplied with one copy each. The

volumes remaining after these demands have been met may be distributed among the geological surveys and geological societies of the United States and of foreign countries, in exchange for their publications.

Section 3. The board may, at its discretion, order the publication of extra copies in addition to the three thousand already provided for. These extra copies shall be placed in the hands of the state geologist. From these, members of the general assembly may, on application, draw up to fifty (50) copies each. Those remaining shall be placed on sale at a price equal to the net cost of printing and binding, which price is to be established by the state supervisor of public printing. The proceeds of such sales shall be accounted for and paid into the state treasury, and the state geologist shall be required by the commission to give suitable bond for the security of the funds thus passing through his hands. The proceeds of such sales shall be credited to the account of the geological survey and shall be used for the prosecution of the further work of the survey without distinction from other funds which the general assembly from time to time appropriates for the survey.

Section 4. The cost of printing, illustrating, electrotyping, binding, et cetera, of said bulletins and said volumes, shall be paid from the general appropriation for state printing.

Section 5. This act shall take effect from and after its passage.

W. S. McKINNON,
Speaker of the House of Representatives.
F. B. ARCHER,
President of the Senate.

Passed May 12, 1902.

THE SURVEY IN ITS RELATIONS TO THE PUBLIC.

The usefulness of the Survey is not limited to the preparation of formal reports on important topics. There is a constant and insistent desire on the part of the people to use it as a technical bureau for free advice in all matters affecting the geology or mineral industries of the state. A very considerable correspondence comes in, increasing rather than decreasing in amount, and asking specific and particular questions on points in local geology.

The volume of this correspondence has made it necessary to adopt a uniform method of dealing with these requests. Not all of them can be granted, but some can and should be answered. There is a certain element of justice in the people demanding such information, from the fact that the geological reports issued in former years were not so distributed as to make them accessible to the average man or community today. The cases commonly covered by correspondence may be classified as follows:

1st. Requests for information covered by previous publications.— This is furnished where the time required for copying the answer is not too large. Where the portion desired cannot be copied, the enquirer is told in what volume and page it occurs and advised how to proceed to get access to a copy of the report.

2nd. Requests for identification of minerals and fossils.— This is done, where possible. As a rule, the minerals and fossils are simple and

familiar forms, which can be answered at once. In occasional cases, a critical knowledge is required and time for investigation is necessary. Each assistant is exepcted to co-operate with the State Geologist in answering inquiries concerning his field.

3rd. Requests from private individuals for analyses of minerals and ores, and tests to establish their commercial value.—Such requests are frequent. They cannot be granted, however, except in rare instances. Such work should be sent to a commercial chemical laboratory. The position has been taken that the Geological Survey is in no sense a chemical laboratory and testing station, to which the people may turn for free analytical work. Whatever work of this sort is done, is done on the initiative of the Survey and not at the solicitation of an interested party.

The greatest misapprehension in the public mind regarding the Survey is on this point. Requests for State aid in determining the value of private mineral resources, ranging from an assay worth a dollar, up to drilling a test well costing several thousand dollars, represent extreme cases. At present there is no warrant for the Survey making private tests, even where the applicant is entirely willing to pay for the service. In many cases individuals would prefer the report of a State chemist or State Geologist to that of any private expert, at equal cost, because of the prestige which such a report would carry. But it is a matter of doubt whether it will ever be the function of the Survey to enter into commercial work of this character; it certainly will not unless explicit legal provisions for it are made.

4th. Requests from a number of persons representing a diversity of interests, who jointly ask the Survey to examine into and publicly report upon some matter of local public concern.—Such cases are not common. It is not always easy to determine whether such propositions are really actuated by public interest or not. Each case must be judged on its merits. The Survey will often be prevented from taking up such investigations by the lack of available funds, while otherwise the work would be attempted.

The reputed discovery of gold is one of the most prolific sources of such calls for state examination. It usually seems wise and proper to spend a small sum in preventing an unfounded rumor from gaining acceptance in the public mind, before it leads to large losses, and unnecessary excitement. The duty of dispelling illusions of this sort cannot be considered an agreeable part of the work of the Survey, but it is nevertheless of very direct benefit to the people of the state.

BULLETIN No. 3.

THE MANUFACTURE OF HYDRAULIC CEMENTS,

BY

ALBERT VICTOR BLEININGER, B. Sc.

LETTER OF TRANSMITTAL.

PROF. EDWARD ORTON, JR., *State Geologist:*

DEAR SIR: — In accordance with instructions received from you I herewith transmit a report upon the Manufacture of Hydraulic Cements.

In this report I have endeavored to develop the principles underlying the processes of cement manufacture in such a manner, that the book might be of some value to the cement manufacturer or cement chemist familiar with the nomenclature of technical chemistry.

I am principally indebted to you for the important suggestions and help given me in preparing this report as well as for the constant consideration and courtesy vouchsafed me. Elsewhere I have expressed my appreciation of the assistance given me by others.

Respectfully submitted,

ALBERT VICTOR BLEININGER.

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PREFACE.

The growth of the American cement industry has been phenomenal. Ten years ago the industry showed but a modest beginning, today it represents many millions of capital. The import of foreign cement which formerly was a great item in our cement consumption is becoming more and more insignificant. But the manufacture of Portland cement is destined to assume still greater proportions as the development in new uses of cement grows and as the younger, now purely agricultural states, turn their attention more towards constructive work.

In spite of the rapid growth in the uses of cement it cannot be said that the financial condition of the industry is flourishing at the present time. To some extent this state of affairs is due to the appearance on the market of new plants who in their eagerness to sell their product, lower the price of cement dangerously close to the cost figure. Again the economic superiority of some plants over others is making itself felt, better equipped plants being able to sell their product cheaper or ship it further than more unfortunate concerns, handicapped by unsuitable location, over-capitalization or inferior mechanical equipment. Thus it behooves the industry to study closely the question of location in regard to the winning of the raw materials, the supply of cheap coal and satisfactory shipping facilities. In Ohio the district comprising the southeastern part furnishing cheap raw materials, cheap coal and excellent shipping would seem especially advantageous for the establishment of an extensive cement industry.

More attention might be paid to the quality of the cement turned out than is now being done at numerous cement works at present. This does not mean that American Portland cements are not, per se, as good as the best Portland cements, since the writer could cite a considerable number of American brands which cannot be excelled, but nevertheless it remains a fact that some cement works are not using the best cement composition possible with their raw materials or are neglecting to pay particular attention to the proper fine grinding of the raw mixture.

Another matter deserving more attention is the preparation of particular cements for particular purposes. Thus for use in sea water, for reservoirs containing water charged with carbonic acid, or soluble mineral salts, cements resisting the various destructive agencies should be produced by grinding the clinker with well burnt silicates, like clay, etc. For building blocks and decorative purposes cements low in soluble salts and low in sulphur should be made and the cement manufacturer should

should cater to the demand for white or colored cement mixtures which is constantly growing. In all such colored mixtures the color should be stable and should not injure the cement. In this manner a demand for higher priced cements answering definite purposes could be built up.

The writer realizes full well the many shortcomings of this report, but hopes that this departure from the usual work on cement manufacture may in some measure be justified. It is very gratifying to be able to record parallel with the mechanical development of the American industry an increasing activity in the field of research which has already given us an honorable position among the world's investigators in this field.

In the preparation of this volume the writer wishes to acknowledge gratefully the assistance rendered him by Mr. S. V. Peppel, B. Sc., author of a report on lime sand brick and the limestone resources of Ohio, and Mr. Samuel Torrey Orton, B. Sc., who was an efficient helper during the summer of 1902. For illustrations and electrotypes acknowledgment is due to the Castalia Portland Cement Co., Castalia, Ohio; Henry S. Spackman Engineering Co., Philadelphia, Pa.; The Allis Chalmers Co., Chicago, Ill.; The Kent Mill Co., New York; The Fairbanks Scale Co., New York; The Williams Pulverizer Co., St. Louis, Mo.; The Bradley Pulverizer Co., Boston, Mass., and others. For assistance in preparing illustrations the writer is indebted to Prof. T. E. French and Mr. Carl B. Harrop.

CHAPTER I.

GENERAL CONSIDERATIONS ON THE HYDRAULIC CEMENTS.

The term cement in its present meaning stands for a mortar which hardens in water as well as in air, in distinction from the air mortars, the ordinary lime mortar, plaster and the so-called Sorel cements. Based on this definition, we know four distinct kinds of hydraulic materials which form the basis of all hydraulic mortars. These are:

1. Pozzuolane cements.
2. Hydraulic limes.
3. Roman cement.
4. Portland cement.

All harden by a process of hydration. They all require water for the initial hardening.

1. Pozzuolane cements are the oldest known hydraulic mortars, having been used by the ancients most extensively, especially by the Romans. The Pozzuolane of the ancients, *pulvis puteolis*, consists of a volcanic tufa, of a porous, open-grained structure which, with the slaked lime, produced the wonderfully durable cement used by the Romans for their gigantic aqueducts and hydraulic work of all sorts. Alone, the pozzuolane materials do not produce a cement, the presence of the slaked lime being invariably necessary. The activity of the volcanic materials depends on the presence of soluble silicic acid, or hydrous silicic acid, which readily enters into combination with the lime hydrate. For this reason any material furnishing silicic acid readily available for reaction with a strong base like lime may be used for this purpose. Even dehydrated silicate of alumina, or lightly burnt clay, will react sufficiently to form with lime hydrate a cement, which has been applied practically by mixing brick dust with slaked lime, resulting in a kind of a hydraulic mortar.

A modern kind of artificial pozzuolane has found extensive application, namely, slag cement, which is made from granulated blast furnace slag ground together with dried quicklime or lime hydrate. Blast furnace slag cooled slowly represents an artificial basic rock with but slight hydraulic properties. When granulated, or cooled quickly from the liquid condition by means of cold water, it possesses the characteristics of the true natural pozzuolane, and has considerable "soluble" or available silicic acid, and when intimately mixed with lime hydrate gives rise to a strong hydraulic cement.

2. The hydraulic limes may be considered as being simply impure limestones, consisting of carbonate of lime intimately blended by nature with clay and some sand. The amount of carbonate of calcium and magnesium is invariably more than 70 per cent. When burnt and made up with water, they slake and gradually harden to a compact mass which attains maximum hardness in water. Owing to their self-slaking, pulverization is unnecessary.

3. Roman cements are likewise naturally blended mixtures of calcium and magnesium carbonates, and clay or earthy matter. The carbonates compose from 50 to 70 per cent. of the mass. On burning they form a porous and friable mass which, however, does not slake in water in the lumpy condition, but must be ground to a powder, which is readily accomplished by means of cheap machinery. The clay content of Roman cement is greater than that of hydraulic limes, the percentage being between 50 and 30 per cent. This limit of composition and the fact that it must be ground distinguishes it clearly from the hydraulic limes. The strength of Roman cement is greater than that of hydraulic lime, though inferior to that of the next higher series, the Portland cements.

4. Highest in the scale of usefulness we find the Portland cements, which, unlike the preceding, are purely artificial materials. In chemical composition they range between 59 and 65 per cent. of calcium oxide, the remainder consisting of the ordinary constitutents of clay, viz., silica, alumina and iron.

In the artificial preparation of this cement the constituents, lime-carrying material of any kind whatever and clay, are mixed and ground together most intimately and burned to a high temperature so that vitrification ensues. The resulting mass is, as a rule, of a dark color, dense and hard. On grinding it to a powder it shows striking hydraulic properties, exhibiting a high tensile and crushing strength and a high cementing power. Both the intimate grinding of the raw materials and the pulverizing of the hard vitrified cement (clinker) stand for a considerable expenditure of power, while the high temperature to be reached in burning means a large consumption of fuel. It is natural, hence, that this cement should be a higher priced mortar material, whose greater cost of production is, however, balanced by the increased strength, uniformity and regularity of its behavior in use.

In these four classes of hydraulic materials we have thus a chain reaching from the raw mixture of hydrous silicious rocks with hydrated lime to the highly calcareous silicates formed at a high heat, approaching igneous fusion, as in Portland cement. From the low tensile strength and low specific gravity of the pozzuolane cement we rise, through the hydraulic lime and Roman cement, to the great strength and high specific gravity of the Portland cement.

In the pozzuolane class the reaction is brought about at the ordinary temperature, and the weakly acid character of hydrous silicic acid is made use of, while in the burning of the Roman cement the strong acidity of anhydrous silicic acid at higher temperatures is made evident, resulting

in the production of a compound corresponding to the type formula $(2CaO)SiO_2$. In the Portland cement reaction the burning temperature is raised still more and hence the acidity of the silica is increased, enabling it to combine with more of the base, and we thus obtain a product corresponding to the type of $(3CaO)SiO_2$. There is no doubt that if a still higher temperature were employed more base could be taken up, chemically and by solution, and a still more complex hydraulic body obtained.

THE CONSTITUENTS OF THE HYDRAULIC COMPOUNDS.

Silicates of lime (or magnesia) constitute the main component of all hydraulic cements of whatever kind. They are, however, invariably associated with alumina or ferric oxide, which either may be assumed to combine with lime, forming aluminates or ferrates of calcium, as in very basic cements, or to enter into the calcium silicate with the formation of a complex calcium-alumina (iron) silicate.

Both the alumina and iron modify the properties of the simple calcium silicates very decidedly; in fact, they may be said to start the hydration reaction, which, without the sesquioxides, would be extremely slow, too slow for practical application. But as the aluminates are also hydraulic in themselves, their hydraulicity is added to that of the silicates and the total strength is thus increased.

In addition to these functions, the alumina and iron decrease the melting point of the compounds, which means, of course, a lower point of vitrification, which is of vital importance in the burning of the highest type of cements.

SILICA AND ITS SALTS.

This highly important compound exists in nature in immense quantities, forming a large part of the earth's crust. It occurs in three principal forms: 1. Crystalline, or glassy, quartz and quartzite. 2. Amorphous, hydrous and anhydrous. 3. Combined in silicate minerals.

It is derived from all of these forms in greater or less degree for use as an ingredient in cements.

Crystalline Silica.—This, in its various modifications, is known as quartz. It is an important constituent of many igneous rocks, and as the silicate minerals of the latter decompose, thus breaking down the rock, the quartz remains unchanged. Its grains, ground down more or less by mechanical abrasion, are removed by running water or wave action, as sand. When deposited in layers and cemented together by various substances like calcium carbonate, ferric hydroxide, etc., they form sandstones. These, in turn, hardened and cemented by still further heat and pressure become quartzite.

The purest forms of quartz crystal are perfectly colorless, having a specific gravity of 2.69, and are very hard. Quartz may be of almost any color, and its structure may be anything from the most perfect crystalline to the decidedly amorphous, as in fused quartz. Quartz is insoluble in all acids, with the exception of hydrofluoric acid. It is attacked, however,

more or less readily, according to the crystallization and size of grain, by caustic potash and soda solutions. In time, finely pulverized quartz unites completely with the caustic bases, forming hydrous silicates of potassium or sodium. When fused with potassium or sodium carbonate it combines readily with these, producing anhydrous silicates, which again are soluble in water.

When quartz is heated to red heat or above, molecular changes take place expressed by peculiar changes in volume, the material expanding, as has been shown by Chatelier, in a seemingly irregular manner.

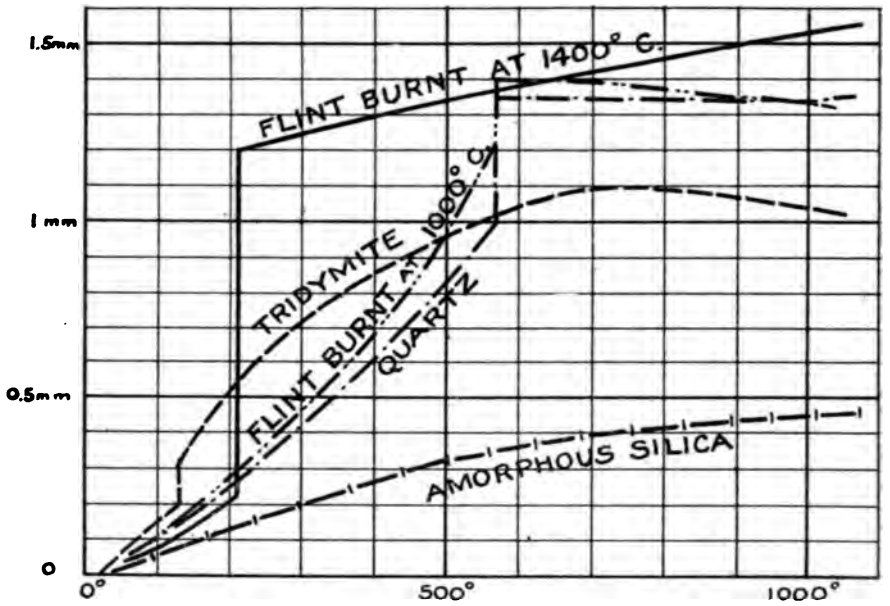

Fig. 1. Chatelier's Curves, showing the expansion of various forms of silica.

These molecular changes, expressed by the expansion, tend to transform the crystalline mass to the non-crystalline or amorphous state. In practical experience this phenomenon is familiarly known in the manufacture of Dinas or silica brick, which are invariably found to increase in volume when exposed to higher temperatures. Likewise in the manufacture of bricks from clay high in sand, which, instead of shrinking, as most clay bricks do, expand in the kiln often to the surprise of the maker. The same fact is applied in the grinding of quartzitic rocks for the pottery industry, which, before being crushed and ground, are calcined and quenched in water while still hot.

But heat assists in bringing about the union of crystalline silica with practically all bases. While the hydrated silicic acid is a most feeble acid, the anhydrous silicon dioxide at higher temperatures becomes the most active and powerful acid, being able to unite with bases in a great number of proportions. In the formation of silicates the physical character of the silica, as well as of the reacting base, is of vital importance in overning the chemical reactions taking place. This refers to the size of

the particles in contact with the basic matter, as well as the crystalline or amorphous condition. While in the discussion of chemical reactions it is always assumed that molecule is in contact with molecule, this ideal condition is never realized except in solutions and fusions. In the manufacture of glass, the sand is ground finely and is intimately mixed with the fluxes, soda and lime. On exposing the mixture to a high temperature the fine particles of silica will be the first to unite with the flux, forming a readily fusible silicate, which later draws the coarser particles into solution. Similarly in preparing artificial silicates from crystalline silica without actual fusion, the first consideration must be fineness of grain. Coarse particles and crystalline fragments are of no value for the reaction. The range of size allowable for the quartz fragments in the preparation of hydraulic mixtures has been examined by the writer in a series of experiments quoted elsewhere. At this stage it suffices to say that quartz grains whose diameter averages more than 0.005 of an inch are practically inert, since their reaction with the basic substance remains only superficial. This question of size is of the utmost importance in practice, since for all artificial cements the quartz must be ground to the required fineness, an operation which means a certain expenditure for power and wear and tear of machinery.

Amorphous Silica.—When quartz is fused with sodium carbonate it dissolves in the latter, forming a sodium silicate readily soluble in water. If we treat the fused mass with water, dissolving it completely, and acidify it we obtain on concentration a precipitate of silicic acid, gelatinous in character. We have thus transformed by fusion the insoluble crystalline silica into the soluble state, for on treating the separated silicic acid with a hot sodium carbonate solution, it will be found to go into solution without difficulty. The colloidal silicic acid, on being brought in contact with hydrated lime, will slowly harden, producing a cement, the substance formed being a hydraulic calcium silicate.

The hydrous silicic acid prepared as above does not correspond to any definite composition, but may be represented by the general formula, SiO_2+xH_2O, the water held chemically being dependent on the conditions of concentration, temperature, acidity, etc., which prevailed during the precipitation of the substance. The chemical activity of the colloid during its hydrous state is proportional to the number of molecules of water fixed chemically, or the amount of water thus held, though silicic acid in no case can ever be considered a strong acid compared with nitric or hydrochloric acids.

Thus we may have the following and many other silicic acids:

H_2SiO_3, meta-silicic acid, bi-valent.

Combining two molecules of meta-silicic acid and imagining one molecule of water split off, we have:

$2H_2SiO_3—H_2O=H_2Si_2O_5$, meta-disilicic acid.

By adding one molecule of water to the meta-silicic acid we obtain further:

$H_2SiO_3+H_2O=H_4SiO_4$, ortho-silicic acid.

As in the case of the meta-acid, we can obtain from the ortho-silicic acid, by splitting off one molecule of water from two molecules:

$2H_4SiO_4—H_2O=H_6Si_2O_7$, ortho-disilicic acid, valency six.

Finally, by the union of one molecule of ortho-silicic acid with one molecule of the ortho-disilicic acid, at the same time splitting off three molecules of water, we have:

$H_6Si_2O_7+H_4SiO_4—3H_2O=H_4Si_3O_8$, tri-silicic acid, tetra valent.

From these five acids all of the natural silicates can be deduced. They may then be said to form the foundation of the great system of silicates, the basis of the clay, glass and cement industries. But the number of compound silicates theoretically possible is very great, and we may say that the different silicates correspond to the equation,

$$xSiO_2+yH_2O=2yH+xSi+(2x+y)O.$$

where x and y are whole numbers.* The number of hydrogen atoms is always divisible by 2, and the number of oxygen atoms is always equal to twice the number of silicon atoms plus half of the number of hydrogen atoms. The following table will illustrate this:

	Formula.	Name.
1.	SiO_2,	Silica, silicon dioxide.
2.	H_2SiO_3,	Meta-silicic acid, valence 2.
3.	H_4SiO_4,	Ortho silicic acid, valence 4.
4.	$H_2Si_2O_5$,	Meta di-silicic acid, valence 2.
5.	$H_6Si_2O_7$,	Ortho di-silicic acid, valence 6.
6.	$H_2Si_3O_7$,	di-basic tri-silicic acid, valence 2.
7.	$H_4Si_3O_8$,	tri-silicic acid, valence 4.
8.	$H_8Si_3O_{10}$,	tri-silicic acid, valence 8.
9.	$H_2Si_4O_9$,	tetra-silicic acid, valence 2.
10.	$H_6Si_4O_{11}$,	tetra-silicic acid, valence 6.
11.	$H_{10}Si_4O_{13}$,	tetra-silicic acid, valence 10.

These hydrous compounds may or may not exist in nature, nor, perhaps, are there anhydrous equivalents produced in the arts, yet the conception of the growth from the acid to the more and more basic compounds must go through the entire scale of silicates and the proper ratios between the RO, R_2O_3 and the acid constituents must be borne strictly in mind. This is illustrated very strikingly by the glasses, and the glazes used in the clay industry which for certain purposes are burnt to different temperatures, each fusing point being fixed by the chemical composition, the ratio of the number of molecules of base to the number of molecules of acid, as well as by the character and number of bases employed. For each one base or one combination of bases combined with silica the fusibility is a function of the base-acid ratio, readily expressed by the oxygen ratio, that is, by the ratio between the number of oxygen atoms in the basic part of the molecule to the number of oxygen atoms in the acid part, as in $CaOSiO_2(CaSiO_3)$ where the oxygen ratio

*Dr. Gustav Rauter, Sprechsaal, Vol. 36, p. 462.

is 1 : 2, or in $2CaOSiO_2$(Ca_2SiO_4) where the oxygen ratio (O.R.) is 2 : 2 or 1 : 1.

Thus in the case of slag compositions showing an oxygen ratio of 1 :1, the resulting slags will be found to be stony in character, melting suddenly and being very liquid, while a blast furnace slag with a ratio of 1 :2 is of a more vitreous character and softens gradually.

Roman cements in general correspond to $2CaOSiO_2$ or an O.R. of 1 :1, while Portland cement approaches closely to $3CaOSiO_2$ with an O. R. of 3 :2.

We see thus that the character of the many silicates which it is possible to produce depends on whether the composition is placed at one or the other end or the middle of the silicic acid series, giving us clays, glasses, slags or cements.

Although the hydrous silicic acids, given in the table above, lose their chemical water at red heat, being converted back into silica (SiO_2), as shown by the reaction:

$$H_2SiO_3+heat=SiO_2+H_2O.$$

the silica under the action of heat will form, according to the amount, number and character of bases and the temperature, salts corresponding to the many possible silicic acids. This fact is repeatedly stated in order to bring out its importance.

As has been said above, the chemical energy of hydrous silicic acid is greater the more water it holds chemically. After the water is expelled, the chemical activity of the acid at the *ordinary temperature* is practically zero, excepting for extremely active bases like potash and soda. It may be said to have become like so much finely ground quartz.

Silica, in the amorphous form, both anhydrous and hydrous, occurs in nature, though not with the abundance and universal distribution which characterizes the crystalline forms. Illustrations of rocks which are used as sources of amorphous silica are chalcedony (which is a mixture of silica and silicic acid), opal, infusorial earth, trass, santorin earth, volcanic ash and pozzuolane. Though not giving rise to cements proper in the modern sense, they furnish an excellent raw material for the manufacture of cements and are especially valuable when used as sand in concrete exposed to sea water, since they unite readily with any uncombined lime. It is in this respect that they have assumed their modern importance in connection with pozzuolane cements.

Combined Silica.—While the elements forming a chemical compound, whether it be a salt of silicic or some other acid, are not viewed by chemists as existing in molecular groups, like SiO_2 or Al_2O_3, and in that sense it is, therefore, improper to speak of silicates as containing silica, still when these substances are used as the raw materials for new combinations like cements or slags, the latter may be attained with as much certainty and ease as if the silica had been supplied in the form of a pure and separate substance. In fact, silicates are exceptionally valuable for form-

ing new silicate compounds from the fact that when one mineral or compound is broken down by heat or other agency, its ingredients are liberated in the nascent state, and will enter at that time into new combinations with a vigor which they possess under no other circumstances. It is, therefore, advantageous to use natural or artificial silicate minerals as raw materials whenever the composition of such minerals lends itself to the matter in hand. For instance, we could use kaolinite, or silicate of alumina (pure clay), in a cement mixture, because both of its components, silica and alumina, are needed in the cement, but we could not use talc, the corresponding silicate of magnesia, because its magnesia would form an undesirable element in the resultant cement.

Also, while it is advantageous to use silicates, where those containing the proper elements are available, it rarely happens that the proportion in which these elements occur are also such as is needed in the compound to be made. For instance, kaolinite furnishes both silica and alumina to the cement-mix to which it is added, but it can be used in limited quantities only, because its proportions of alumina are high and the silica relatively low. If enough were used to bring in all the silica desired, the resultant cement would be overloaded with alumina. Thus there is this obstacle to the free use of the silicates in producing new silicate compounds, and it is, therefore, generally necessary to obtain the desired composition by mixture of different silicates or more commonly by supplying the extra silica needed in one of its free or uncombined forms.

ALUMINA AND FERRIC OXIDE.

We have now discussed the various sources of silica, the crystalline, amorphous and combined, and have shown how the kind of silica influences the silicate reaction and how complex silicates are built up in the heat reactions with which we are dealing, based on the conception of the hydrous polysilicic acids. But silicates of calcium oxide or magnesium oxide alone would not do the work required of mortars. Of the great numbers of such silicates prepared by the writer, none of them showed the strength of even weak cements, but remained soft and friable; in water they often crumbled, and yet by the very preponderance of the silica in cements the calcium silicate must be the main hydraulic agent. But it is evident that the alumina must play an important role in causing the hydration reaction to take place in the manner which we know in cements.

In order to show how alumina affects the hydration of cements it is perhaps best to indicate how alumina behaves when united with calcium oxide alone. Prof. Zulkowski*, thus found that a mixture of calcium oxide and alumina corresponding to the formula $CaO.Al_2O_3$, burnt for eight hours when mixed with water, set in two minutes and hardened to a very hard mass over night; in three months it became so hard that it could hardly be scratched with a knife. A mixture of the formula $2CaO.Al_2O_3$, heated to vitrification also hardened with great rapidity in

*Sonderabdruck aus "*Die Chemische Industrie*," 1901

two to three minutes and assumed an extraordinary hardness after being in water for three months. We see hence that the alumina-lime compounds play an important role in the economy of the cementing process. They accelerate the reaction and contribute strength.

Thus the American investigators, S. B. and W. B. Newberry*, obtained practically the same result. The mixture $2CaOAl_2O_3$, when made to a mortar with water, set very rapidly in a few seconds and became extremely hard.

The experimental work in the investigation of the alumina-lime compounds has been carried on by many chemists like Winkler, Chatelier, Michaelis, Newberry, Rebuffat and others.

As we have seen, the most readily available source of silica for cement making is clay which invariably introduces a certain amount of alumina with every part of silica, it being, as we know, an aluminum silicate. If we were to take a pure clay, kaolinite, and mix it with enough lime to make, say, a bisilicate and a bicalcium aluminate we would obtain on burning a hydraulic cement which would harden well, but too rapidly. The rapidity of setting of this cement is due to the high content of alumina and is a source of danger, as the cement in practical use would show a dangerous tendency of cracking. We see thus plainly that the alumina must be kept low so as to keep the cement within safe limits, but it must always be present.

Zulkowski prepared a cement from Zettlitz kaolin ($Al_2O_32SiO_22H_2O$) corresponding to the formula $2(2CaOSiO_2)$ $(2CaOAl_2O_3)$. On burning this mixture to vitrification a white porcelain-like body was produced which, when powdered and mixed with water, set in fifteen minutes. After ninety minutes the cement became extremely hard and after a few months it was found to be still harder. Zulkowsky did not test this cement for constancy of volume. By the addition of quartz he prepared other white cements with the same lime-silica ratio ($2CaOSiO_2$), which were all excellent cements.

These examples have thus shown clearly the necessity of having alumina present in cements. Just what the exact chemical function of alumina is cannot be discussed here at this stage, but the discussion must be postponed to a later part of this work.

The Function of Ferric Oxide.—Chemically, iron is the natural substitute of aluminum, which is shown by the fact that it forms different hydrates corresponding to the various hydrates of aluminum. The first conclusion would hence be that ferric oxide behaves similarly to alumina when combined with lime, or with lime and silica. Many investigators have searched into this relation with different results and conclusions.

Zulkowsky again has made experiments in this direction in the most careful manner, and as his results check with those of the most noted

*The Constitution of Hydraulic Cements, *Journal Society Chemical Industry*, November 1897.

investigators they may be selected as representing the characteristic behavior of ferric oxide.

On burning the mixture $CaOFe_2O_3$ in the Seger furnace till partially fused it assumed a graphite-like appearance, and when ground and mixed with water it formed a pat of a fine mahogany-like color. It set in four hours. After five hours more it was hard enough to be placed in water. After several months the pats became quite hard, but did not show as much strength as the corresponding alumina compound. The mixture $(2CaO)Fe_2O_3$, burnt to softening, which took place at a white heat, showed a decided crystalline structure. After grinding and making up with water the pats set in fifteen minutes and in one to two hours had become quite solid and hard. After one week in water they softened somewhat and lost their original strength. When dried in a dessicator they became harder again, but did not reach the hardness of the corresponding alumina compound. More favorable results were obtained with impure materials, that is, with reagents containing some silica and alumina.

We can say, therefore, that the iron-lime compounds are very similar to the alumina-lime products, though much more feeble in their hydraulic reaction. One function in which iron is more effective is the greater fusibility produced by it. While a lime silicate like $(3CaO)SiO_2$ is practically infusible excepting in the electric furnace and the oxy-hydrogen blowpipe, it is at once rendered more fusible by the addition of alumina and much more fusible by adding ferric oxide. This is observed quite strikingly in using as the clay base a pure clay, like kaolin, or an impure variety containing more or less iron. Only by the presence of iron is it possible to burn Portland cement at commercially feasible temperatures. In addition the oxides of iron seem to counteract the phenomenon known to the cement men as "dusting," and of late the surprising resisting power of ferruginous cements to the action of sea water has aroused general attention.

LIME.

This important material, which constitutes the greatly preponderating ingredient of all hydraulic cements, occurs in nature in enormous quantities, chiefly as calcium carbonate, from the almost chemically pure form of calcite and aragonite, in various degrees of purity, down to the loamy and impure marl clays. Pure calcium carbonate consists of 56 parts calcium oxide and 44 of carbon dioxide, which begins to be expelled at about 600° C., the evolution of the gas being completed at 1040° C. in all limestones. The harder, more dense and crystalline the carbonate of lime is the slower and more reluctantly will the carbon dioxide be evolved. By the presence of silica or silicate of alumina the decomposition of the carbonate is accelerated, and hence more impure limestones are easily overburnt, as the practical lime burner says.

Calcium carbonate is dimorphous, crystallizing as calcspar in the hexagonal and as aragonite in the rhombic system. Calcium carbonate is nearly insoluble in water, 1,000 grams of water dissolving .0018 gram of the compound, but it is more soluble in water containing carbon dioxide; 1,000 grams of water charged with this gas will dissolve, at 0°C.,0.7 gram of calcium carbonate; by increasing the pressure 3 grams of the carbonate may be dissolved. This calcium salt is readily decomposed by inorganic and even weak organic acids with the evolution of carbon dioxide. When exposed to higher temperatures the calcium carbonate is decomposed according to the reaction:

$$CaCO_3=CaO+CO_2.$$

On enclosing a piece of calcium carbonate in a tube and connecting the latter with a mercury manometer it is found that for every temperature the evolution of the carbonic acid gas remains stationary at a certain pressure, no more calcium carbonate being decomposed. This was shown experimentally by Le Chatelier,* who thus determined the dissociation tensions of calcium carbonate for a number of temperatures, which are shown in the accompanying table:

Dissociation of Calcium Carbonate.

Temperature.	Pressure.	Temperature.	Pressure.
547° C.	27 mm. Mercury.	745° C.	289 mm. Mercury.
610 "	46 " "	810 "	678 " "
625 "	56 " "	812 "	753 " "
740 "	205 " "	865 "	1,333 " "

The reaction is a reversible one; that is, carbon dioxide is reabsorbed as soon as the tension of the gas approaches the dissociation tension at the given temperature and calcium carbonate is again formed. This point is well illustrated in limekilns where it is observed that when the draft of the kiln is sluggish and the temperature low the calcium oxide, being surrounded by the carbon dioxide, reverts to calcium carbonate.

The decomposition of calcium carbonate is accelerated by the presence of steam, so that the burning temperature is reduced greatly. Professor Herzfeld has made extensive experiments with the use of superheated steam and has proven that it affords an excellent means of producing a high grade porous calcium oxide.

*Compt. rend. 102 1233 (1886.)

His results are given in the following table:

Temperature.	500°C.	650°C.	660°C.	790°C.
Per cent. of Calcium Oxide in limestone burnt in steam.....	0	7%	23%	100%
Per cent. of Calcium Oxide in limestone burnt in air.....	0	0	0	37%

The impurities contained in limestone accelerate the rate of decomposition, this being especially true of silica. At 1000° C. 8 per cent. of silica causes the lime to be overburnt owing to the formation of a calcium silicate. The higher the temperatures the greater will be the effect of any silica present. The same thing may be said of alumina and iron, though these are less energetic in their behavior. Pure lime burnt from calcium nitrate at 1300° C. hydrates extremely slowly; burnt at 1600° C., the calcium oxide is crystalline and can be hydrated, but not slaked, showing hydraulic properties. Somewhat below 1600° C. it forms a porcelain-like mass of great density. In the electric furnace calcium oxide sublimes at a temperature corresponding to about 3000° C., melting and boiling between the electrodes. The condensed sublimed matter forms beautiful crystals of calcium oxide. The thermal reaction of the decomposition of calcium carbonate is as follows:

$$CaCO_3 + 437.41 Cal. = CaO + CO_2.$$

or 1 gram of calcium carbonate requires 437.4 gram calories for its decomposition. One pound of the carbonate of lime would thus require the heat of 0.06 pound of average Ohio coal, taking 7,000 calories as the calorific value of the fuel.

The calcium oxide, as we know, on being brought in contact with water eagerly combines with the latter, forming calcium hydrate according to the reaction:

$$CaO + H_2O = Ca(OH)_2 + 15100 \text{ cals.}$$

This is seen to be an exothermic reaction, one gram of the calcium oxide evolving 269.6 calories. The hydration is accompanied by an increase in volume. While the specific gravity of the calcium oxide varies from 3.08 to 3.18, that of the hydrate is 2.078. The increase in apparent volume of the oxide on being changed to the hydrate is about 3½ times the original volume if just enough water is added.

This explains the injurious action of lime in cement or bricks and other clay ware, the body containing the lime being destroyed by the hydration as soon as water is being absorbed. The increase in the volume of the oxide depends to a great extent on the manner of slaking; that is, on the amount of water used. Lime hydrate is decomposed into calcium

oxide and water at red heat. Its solubility in water at the ordinary temperature is 0.14 parts, at 100° C. half of this amount. Lime is dissolved more readily by a sugar solution, or glycerine, or an alcoholic iodine solution.

Calcium oxide absorbs carbonic acid eagerly, especially at higher temperatures. On heating calcium oxide in a bulb to redness, removing the lamp and conducting carbon dioxide into the bulb in a strong current, it will be found that the lime becomes red hot in a few seconds, continuing to glow for fifteen minutes owing to the energetic absorption of the carbonic acid.*

All these facts tend to show that lime is a very powerful base, combining with acids with the greatest ease. Not only higher temperature, but also lower ones may bring about the union of silica and lime. When a mixture of quartz and lime hydrate is exposed to steam at a pressure of about 120 pounds to the square inch a reaction between them takes place; a hard, artificial sandstone is produced. This is the basis of the sand-lime brick industry.

The varieties of rocks and minerals which are used as a source of carbonate of calcium will be discussed in the next chapter. Beside the carbonate, there are a few other lime compounds having a more or less important use in this same connection.

Gypsum, composed of one molecule of calcium sulphate and two molecules of water, is a possible but not a probable source. Its value for other purposes is too great to make it applicable for cement-making; besides, it would offer difficulties in manufacture which would be hard to overcome. The complete expulsion of the sulphuric acid would be a difficult task and the liability of retaining sulphur in some shape in the cement too great. Gypsum is used in the cement industry, but not in direct connection with the cement burning itself.

Though slag from blast furnaces is a source of calcium oxide, in a way, it is united with so much silica and alumina that it must be considered as furnishing silica rather than the base.

In some processes of the chemical industries calcareous waste products may be used for the manufacture of cement. This applies especially to the manufacture of soda by the Solvay process, were calcium chloride becomes available for cement making in large quantities. This material is chemically well suited for the purpose, since the chlorine is expelled with comparative ease.

Dolomite.—The double carbonate of calcium and magnesium is known as dolomite. Its percentage composition when pure is 54.35 per cent. calcium carbonate and 45.65 per cent. magnesium carbonate.

Like limestone, it is subject to the same variations in composition and physical properties, as we have hard, compact dolomites as well as

*Raoult, Compt rend. 92, pp. 189 and 1111.

soft, marl-like dolomitic materials. But the relative proportions between the magnesium and calcium carbonate vary greatly, so that we start from practically all calcium carbonate to the dolomitic proportions 54.35 calcium to 45.65 per cent. magnesium carbonate. The specific gravity of dolomite is from 2.8 to 2.95; the hardness of the compact rock is greater than that of limestone and it is distinguished from the latter in that it is much less readily soluble in cold hydrochloric acid. Some of the hard dolomites show a distinct fissured structure. Sometimes dolomite is found in beds formed by direct deposition as the precipitate from saturated water, or it may be found replacing original deposits of limestone. As a cement material it is not promising, since it gives rise to two silicates (of lime and magnesia) which have different rates of hydration and which hence interfere with each other in the hardening process, unless the burning took place at a low temperature not over 1000° C. In nature we find dolomitic hydraulic materials in the form of the natural cement rocks, like the Rosendale, Louisville, Utica and Milwaukee. But all of these must be burnt at a low temperature, at which not all of the calcium carbonate has been decomposed.

MAGNESIA.

This substance is chiefly derived from magnesite, magnesium carbonate, which is closely analogous to calcium carbonate in all its properties. It crystallizes as rhombohedral crystals, isomorphous with calcite. Its decomposition, however, takes place at a considerably lower temperature than that of calcite, carbon dioxide being evolved at a lively rate at about 500° C. Magnesium exhibits a great tendency to form basic and hydrated carbonates, whose compositions vary with the conditions of precipitation. On heating magnesium solutions to higher temperatures, subjecting them to higher pressures or evaporating them to dryness, the normal carbonate is formed.

The mineral hydromagnesite is a basic carbonate of the composition $3MgCO_3Mg(OH)_2 3H_2O$. Artificially prepared magnesium carbonates are usually bulky, very light precipitates. From boiling solutions a denser basic carbonate is obtained than from cold ones. In nature we find magnesium carbonate as a dense, usually white, mineral. On burning this first loses its carbon dioxide and begins to shrink in volume quite decidedly, continuing to do so up to very high temperatures.

Magnesium oxide slakes on contact with water and shows some increase in volume, but this increase is much less than that of the calcium oxide converted into calcium hydroxide.

The hydration of magnesium oxide is itself associated with hydraulic activity, that is, magnesium oxide prepared at a low temperature when made up with water will harden and form a tolerably strong cement, as was found to be the case by Deville and others. Magnesium silicates and aluminates show decided hydraulic properties. Thus Fuchs was able to

produce a very hard cement by burning talc at a very high temperature. Lieven also claims to have produced well hardening cements by igniting a mixture of one equivalent silica with one equivalent of magnesia. Rivot* says that magnesium silicates behave similarly to the lime compounds, while Held was not able to produce any hydraulic compounds from magnesia minerals and artifically prepared silicates. Kawalewsky again reports on vitrified magnesia cements which after ten years were still found to be sound and which had shown high tensile strengths. Zulkowski prepared the dimagnesium silicate and found it to show hydraulic properties, setting in two hours to a hard, earthy mass. After two months in water it attained moderate hardness.

**S. B. and W. B. Newberry came to the conclusion that magnesia shows no hydraulic properties when heated with silica, alumina or clay, and says that it probably plays no part in the cement reaction. Hence these investigators claim that magnesia cannot replace lime in cement mixtures.

Sorel Reaction.—Magnesium oxide burnt at a low temperature, mixed with solutions of salts, like magnesium chloride or calcium chloride, produces extremely hard though usually slow-setting cements, used to some extent in fastening brass to glass as in lamps, laying floor or wall tiles, or similar purposes. Cements of this type are called Sorel cements and include also similar mixtures, like calcium oxide and calcium sulphate, anhydrous gypsum made up with a solution containing Glauber's salt or potassium sulphate and others. The last named mixture even is hydraulic in character and is extensively used for making floors in place of Portland cement being known as Estrich or Mack's Cement. The Sorel reaction depends on the formation of basic double salts, as a rule very insoluble in character. Kosmann† attributes the formation of these compounds to the so-called chemical residual energy. Though the chemical valency of many compounds is satisfied they have not yet lost all chemical activity, in fact, many of the so-called neutral salts may be considered as unsatisfied compounds. This seems to be shown by their thermo-chemical behavior. It is found that outside of the heat produced by the combination of acids and bases there is still some heat left which represents a certain chemical energy. This heat is called by investigators the residual chemical energy which enables the so-called neutral salts to take up water in chemical combination as well as to add, in place of water, salts or oxides to the molecular structure. All of the salts of strong acids and bases are caustic in nature, which is shown by their tendency to take water from other salts. Examples of this kind are cupric sulphate, lead chloride, cupric chloride, sodium carbonate and many others. This caus-

*Wagner's *Jahresbericht*, 1856, p. 181

**The Constitution of Hydraulic Cements. *Journal Society Chem. Industry*, Nov. 1897.

†Transactions, Deutscher Verein fuer Ton, Cement und Kalk-Industrie, 1900.

tic effect is due to the residual chemical energy. Basic salts are produced simply by the substitution of oxides in the place of water taken up. Thus lead chloride takes up two molecules of water: $PbCl_2H_2(OH)_2$, while magnesium chloride unites with six molecules of water: $MgCl_2H_6(OH)_6$.

The chemical energy shown by the hydration of these compounds may take the form of uniting with as many molecules of another compound as it has taken up water; or, the water may be replaced by an oxide like magnesium oxide, calcium or barium oxide, so that there is produced a basic compound like $MgCl_23MgO$, this being the formula of the Sorel cement, named after the inventor, who made the discovery in 1867.

This extraordinary ability of such compounds to form basic salts Kosmann illustrates by the many natural compounds existing which closely follow the formula of basic salts. He mentions:

Hydrous Magnesite	$3MgCO_2Mg(OH)_23H_2O$
Malachite	$CuCO_3Cu(OH)_2$
Basic zinc carbonate	$ZnCO_32Zn(OH)_2$
Clay	$Al_2O_32SiO_22H_2O$
Serpentine	$3MgO2SiO_22H_2O$
Willamite	$ZnSiO_3ZnO$.

Magnesite as such is at present not available in large quantities in the United States, it being imported chiefly from Greece and Syria. Hence its cost would be too great for production on a large scale at this time. It owes its importance to its refractoriness, being a valuable basic heat-resisting material. Its drawbacks in this connection, however, are its great brittleness and its tendency to crumble when exposed to temperature fluctuations as well as its marked conductivity of heat.

CHAPTER II.

RAW MATERIALS OF THE CEMENT INDUSTRY.

In this chapter will be taken up the various raw materials of the four kinds of hydraulic cements, taken in the order of the classification adopted, which brings the highest class of cements as the last and most complex of the series.

RAW MATERIALS FOR POZZUOLANE CEMENT.

In the oldest type of hydraulic pozzuolane materials we have as the main constituent a substance containing hydrous silicic acid which on the simple addition of slaked lime becomes a hydraulic cement. These materials show extreme variety in composition and physical behavior. Modern metallurgical processes furnish us in addition artificial pozzuolanes which are finding application as valuable cement materials. We can thus distinguish natural and artificial pozzuolanes.

We have no natural pozzuolanes in Ohio, and yet they deserve some discussion due to the fact that as an addition to Portland cement for work in sea water they have shown valuable properties. Owing to the great solvent action of sea water on concrete, the question of the life of cement work has become an extremely important one. There is no doubt but that some concrete work exposed to sea water has suffered considerably, and the knowledge of the fact has caused apprehension on the part of engineers, many of whom still look with suspicion upon cement as a proper material to be subjected to the action of sea water. Since the capital involved in concrete construction of this kind is enormous, it has become a vital task to users as well as sellers of cement to study the behavior of this material under various conditions and to devise means of improving it when necessary.

The principal natural pozzuolanes are pozzuolane proper, trass and santorin-earth. All of these when mixed with slaked lime harden and form a hydraulic mortar.

The pozzuolane proper is a hydrous, volcanic, porous rock whose specific gravity is from 2.3 to 2.55, found in Italy, especially near the

Vesuvius and at Bacoli, as well as at Montenuova. It is partly soluble in hydrochloric acid. The composition of two typical pozzuolanes is:

	Per cents.	
	I*	II**
Silica	47.85	73.00
Alumina	17.35	11.90
Ferric Oxide	9.75	1.55
Lime	10.00	0.65
Magnesia	3.90	.....
Loss on ignition	6.10	4.30
Alkalies, etc	4.70	8.45
Silica soluble in caustic potash	15.70	12.40
Silica soluble in sodium carbonate solution	2.30	2.00

*Feichtinger, Chemische Technologie der Moertelmaterialien.
**R. Feret, Tonindustrie Ztg. No. 15, Vol. 25.

No. I is an Italian pozzuolane. No. II is found in Nebraska. Typical analyses of trass and santorin earth are as follows:

	Per cents.	
	Trass.	Santorin Earth.
Silica	59.75	65.55
Alumina	18.05	14.60
Ferric Oxide	3.70	4.10
Lime	1.90	3.70
Magnesia	0.65	0.95
Loss on ignition	7.00	4.25
Alkalies, etc	8.85	6.50
Silica soluble in caustic potash	17.30	14.00
Silica soluble in sodium carbonate solution	1.00	2.00

*R. Feret, Ton. Ztg. No. 15, Vol. 25.

Trass also is a kind of volcanic tufa, it being consolidated volcanic dust which has been subjected to the action of pressure and water. It is found in large quantities in the Rhine province, Germany, the top layers being loose in structure, the lower rock-like. Trass, like pozzuolane, is partly soluble in hydrochloric acid and contains water of hydration.

Santorin-earth is found on the Island of Santorin and is likewise a kind of volcanic material, like pumice-stone, but is softer than the two preceding materials. It differs in its high content of free amorphous silica; it is not so easily decomposed by acids and does not gelatinize. About one-fifth of the Santorin-earth is supposed to be pumice stone.

ARTIFICIAL POZZUOLANES.

Similar to the natural pozzuolane rock products, we can produce such materials artificially, and the two most important pozzuolane substances of this kind are the slags and the dehydrated clays.

Slags.—The slags used for this purpose are the waste products of the blast furnaces smelting iron from its ores. Slags from the refining of pig iron, or the manufacture of steel, or from the manufacture of other metals than iron are not used.

The slag as it leaves the furnace is converted into a true pozzuolane by being quenched in cold water while still in the hot liquid condition. But not every slag is available for hydraulic purposes. Several factors, of which the most important is the composition, govern the properties of the material. Tetmayer* in his extensive and thorough examination of the subject says the following in regard to the composition of suitable slags:

"The hydraulic activity of a slag depends in the first place on its basic character expressed sufficiently by the ratio of the lime to the silica. All slags corresponding to a ratio of

$$CaO : SiO_2 < 1.00$$

are not suitable for cement making. The most favorable ratio of lime to to silica and to alumina is approximately

$\%CaO : \%SiO_2 : \%Al_2O_3 = 46 : 30 : 16 = 1.00 : 0.65 : 0.35$ or $CaO : SiO_2 + Al_2O_3 = 1.00 : 1.00$.

Magnesia is not a desirable constituent of slags and should be as low as possible. A high content of sulphur is very objectionable and for best results the content of sulphur should not be more than 1.25 per cent. With the same composition the greenish gray, more glassy, slag from gray iron is to be preferred to the yellowish foamy material. In the granulating process this slag should be as thin liquid as possible and the water used in quenching quite cold.

*Resultate Spezieller Untersuchungen auf dem Gebiete der Hydraulischen Bindemittel page 152.

Blast furnace slags are bodies closely akin to glasses and might be considered alloys in character. It is, of course, evident that the composition of the slag is dependent on the compositon of the ore as well as on the kind of pig iron it is desired to produce. If the ores used are uniform in character, the slag produced will also be regular in composition as long as the same grade of iron is being made. It is obvious that an ore high in silica will require more limestone for fusion than one lower in this constituent; an increase in the sulphur or phosphorus in the ore will also necessitate an increase in the lime content of the slag. The foundryman in trying to smelt iron cheaply and yet maintain a good quality is certain to make a slag of a variable composition. Since the slag is the by-product, it is of importance only so far as its composition and fluidity affect the working of the furnace and the quality of the iron. Some limitations are met, however, in the fluctuation of the slag, as it will not melt and flow freely, if its composition departs too far from the usual range. Thus it is often impossible to remove all the impurities, sulphur and phosphorus from the iron, as the high content of calcium necessary would make the resulting slag too refractory. If the slag is to be used for the manufacture of slag cement, proper allowance must be made for the fluctuations in the composition resulting from the variations in the composition of the ore. Slag of improper composition should be rejected for the making of pozzuolane cement, though it may be used for the manufacture of slag brick. The rules of Prof. Tetmayer, given above, which he has deduced from a great number of analyses and experiments, will serve as a guide for the selection of a slag.

In the tables on pages 45 and 46 are given the analyses of a number of European blast furnace slags which were made the subject of an investigation pertaining to slag cements by Prof. L. Tetmayer,* excepting No. 21.

Prof. Tetmayer also made an elaborate series of tests with these slags in the granulated condition by grinding them together with various amounts of hydrated lime and testing them for tensile and crushing strengths. These results, representing mixtures with 15 per cent. of lime, are plotted in the accompanying curve, figure No. 2.

These results seem to show that the general tendency of the slags is to correspond to the Tetmayer ratio, although this fact is brought out by no means sharply. We must remember, however, that other factors enter into the resulting strength of slag cements, such as the degree of liquidity, the degree of granulation of the slag, etc. Until additional experimental data are collected the results of Tetmayer must, as a whole, be accepted. Prost and Mahon take exception to his limits with reference to the alumina, as they have obtained good results with higher alumina contents.

*L. Tetmeyer: *Resultate Specieller Untersuchungen Hydraulischer Bindemittel, Zuerich* 1887.

Number.	Per cents of Ingredients.							
	Silica.	Alumina.	Ferrous Oxide.	Manganous Oxide.	Calcium Oxide.	Magnesium Oxide.	Calcium Sulphate.	Calcium Sulphide.
1	35.07	4.99	1.13	7.63	40.73	4.28	1.72	2.18
2	39.59	9.07	0.64	5.12	34.89	11.66	.....	2.28
3	27.31	22.40	1.36	.....	47.00	0.42	0.12	1.39
4	34.33	11.01	1.73	.....	49.78	0.93	.....	2.16
5	27.98	19.69	0.30	.....	44.64	4.76	0.03	2.61
6	33.16	11.93	1.47	.....	48.63	1.03	.....	3.79
7	39.95	14.98	0.34	.....	40.46	1.62	0.24	1.99
8	34.77	7.71	0.70	0.34	49.17	2.02	0.65	2.29
9	30.55	13.63	0.43	0.34	48.06	3.27	0.48	3.20
10	35.11	17.43	0.24	2.61	39.76	4.32	0.27	2.28
11	32.51	13.91	0.48	0.60	44.75	2.20	0.64	4.90
12	32.79	18.25	0.82	2.77	39.16	4.33	0.51	1.46
13	30.81	17.55	0.60	2.43	42.30	4.35	0.29	1.77
14	29.91	20.49	0.84	1.31	39.83	3.31	0.96	1.99
15	27.86	22.05	1.28	0.50	39.17	4.23	0.10	2.86
16	28.33	13.81	1.44	0.50	46.66	5.44	.....	3.82
17	31.90	18.40	0.99	2.27	40.27	4.46	0.14	1.64
18	30.49	17.15	0.70	1.65	44.29	4.48	.....	1.11
19	32.17	17.84	0.74	.....	43.79	2.19	.....	2.27
20	28.73	22.87	0.96	.....	39.94	4.51	0.16	3.23
21	32.20	15.50	.....	.....	48.14	2.27	.....	....

$\frac{\%CaO}{\%SiO_2}$	$\%CaO : \%SiO_2 : \%Al_2O_3$	Oxygen Ratio (Molecular) $CaO : Al_2O_3 : SiO_2$	Specific Gravity.	Loss on Ignition.	Remarks.	Number.
1.16	1 : 0.86 : 0.12	1.25 : 0.25 : 2	3.09	0.59		1
1.07	1 : 0.93 : 0.26	1.15 : 0.48 : 2	3.17	2.80		2
1.72	1 : 0.58 : 0.48	1.84 : 1.44 : 2	2.88	0.08		3
1.45	1 : 0.69 : 0.22	1.59 : 0.57 : 2	2.96	0.90		4
1.60	1 : 0.63 : 0.44	1.70 : 1.23 : 2	2.94	0.05		5
1.47	1 : 0.68 : 0.25	1.58 : 0.56 : 2	2.90	2.09		6
1.01	1 : 0.99 : 0.37	1.08 : 0.66 : 2	2.85	0.41		7
1.41	1 : 0.71 : 0.16	1.51 : 0.39 : 2	2.94	1.94		8
1.58	1 : 0.64 : 0.28	1.67 : 0.78 : 2	2.89	2.79		9
1.20	1 : 0.83 : 0.44	1.29 : 0.93 : 2	2.81	5.05		10
1.38	1 : 0.73 : 0.31	1.47 : 0.75 : 2	2.85	3.17		11
1.19	1 : 0.84 : 0.47	1.28 : 0.99 : 2	2.89	0.25		12
1.37	1 : 0.73 : 0.41	1.47 : 1.14 : 2	2.92	0.42		13
1.33	1 : 0.75 : 0.51	1.43 : 1.20 : 2	2.89	1.06		14
1.40	1 : 0.71 : 0.56	1.51 : 1.38 : 2	2.93	0.31		15
1.65	1 : 0.61 : 0.30	1.76 : 0.87 : 2	2.94	3.08		16
1.26	1 : 0.79 : 0.46	1.36 : 1.02 : 2	2.87	0.37		17
1.45	1 : 0.69 : 0.39	1.55 : 0.99 : 2	2.91	0.58		18
1.36	1 : 0.73 : 0.41	1.47 : 0.99 : 2	2.91	0.25		19
1.36	1 : 0.74 : 0.59	1.45 : 1.41 : 2	2.88	0.48		20
1.49	1 : 0.67 : 0.32	1.62 : 0.85 : 2			American cement slag	21

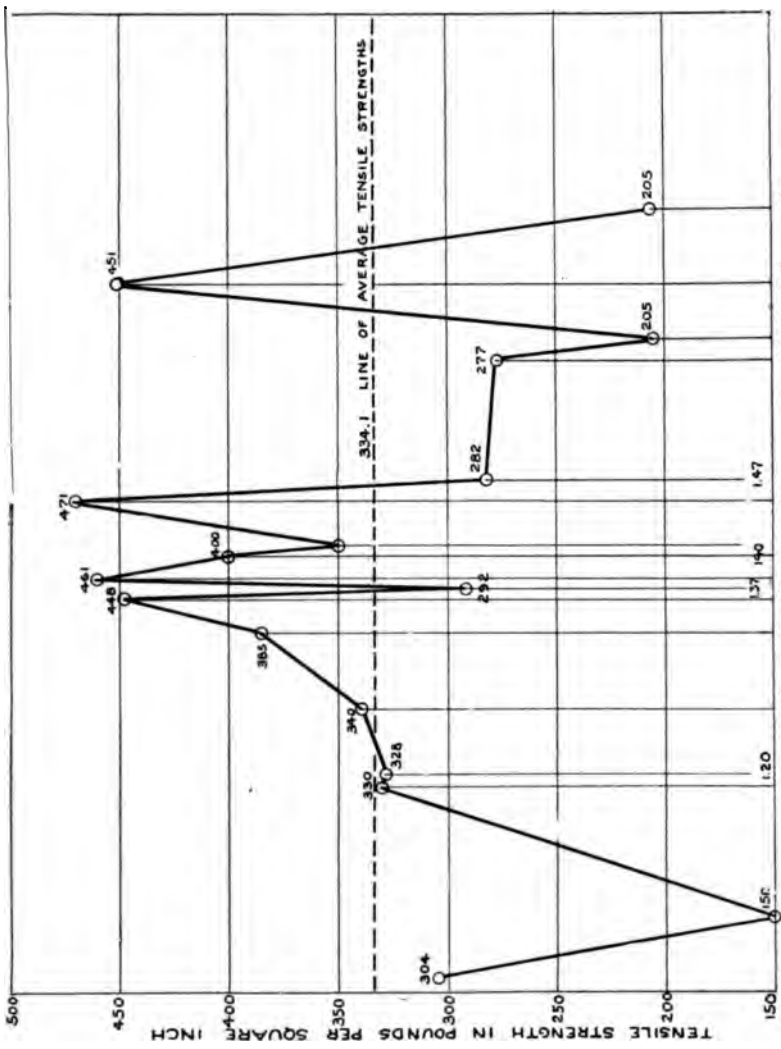

Fig. 2. Tetmayer's Curve, showing the tensile strength of various granulated slags, with 15 per cent. of calcium hydrate tested after 28 days in water.

Principles of Slag Formation.—The formation of slags has received great attention for a long time by metallurgical chemists. The principles of their formation and the methods used in their study are identical or closely analagous to the formation and study of cement silicates, and for that reason the following resume has been prepared.

Beside the proper chemical composition of the slag which is necessary to remove the detrimental constituents of the ore by fusion the melting point of the slag is of extreme importance as well as the degree of liquidity on fusion.

For purposes of comparison it might prove of value to marshal the different possible silicates in a table so that their relations to each other may be understood in which "RO" stands, in general, for any base, like calcium oxide, magnesium oxide, barium oxide, etc.:

Name of Silicate.	Molecular Formula.	Oxygen Ratio.
Tri-silicate.....	$2RO\ 3SiO_2$	2 : 6 = 1 : 3
Bi-silicate.....	$RO\ SiO_2$	1 : 2
Sesqui-silicate.....	$4RO\ 3SiO_2$	4 : 6 = 2 : 3
Singulo-silicate.....	$2RO\ SiO_2$	2 : 2 = 1 : 1
Subsilicate.....	$3RO\ SiO_2$	3 : 2

We observe that the names of the silicates are derived from the oxygen ratio which has been universally accepted as the metallurgical nomenclature.

According to Ledebur, the bi-silicate of calcium is the most fusible compound, the temperature rising with an increase in lime or silica. The singulo and tri-silicates fuse only at a very high temperature, while the subsilicate is infusible excepting in the electric furnace and in the oxy-hydrogen flame. The magnesium silicates are all difficult to fuse and do not show such decided differences in their melting points as the calcium silicates. Of the lime-magnesia silicates (one molecule of CaO to one molecule of MgO) the bi-silicate is, according to Berthier, the most fusible one, while the tri-silicate is the most infusible.

The presence of alumina modifies the melting point of a slag considerably, the most fusible lime-alumina silicate being, according to Bodemann*, a bi-silicate approximately $4CaSiO_3+Al_2Si_3O_9$. Berthier found that all lime-alumina silicates are most fusible when the amount of alumina is about one-third of that of lime, by weight, it being equal to 1 equivalent of alumina for 6 equivalents of lime or 102 parts by weight of alumina to 336 parts of calcium oxide.

The same investigator found that an increase in the lime content causes the melting point to rise only very gradually, but rapidly as soon as the alumina is increased, so that silicates with the molecular ratio of 1 equivalent of alumina to 3 equivalents of calcium oxide are still fusible, while with a ratio of 2 alumina to 3 of lime the slags are almost infusible.

Beside the melting point proper, we must consider the degree of liquidity or the viscosity of the slag on melting. The slags melting at the lowest temperatures are not always the most liquid ones. The slower the transformation from the solid to the liquid condition the more viscous and "tough-liquid" will the slag be. Slags high in silica and also those high in magnesia or alumina show this property quite strongly and hence are as unfit for the purposes of iron manufacture as slags with too high a melting point. In a slag of proper composition the fusion takes place

*Bodemann, Probirkunst, p. 251.

suddenly and the resulting liquid slag is not viscous. Alumina especially is a strong agent towards producing viscosity.

Prof. N. W. Lord defines the limits of slag composition by a very convenient diagram:

	Calcareous $6ROAl_2O_3$	
$2ROSiO_2$		$ROSiO_2$
Singulo Silicates	Area of	Bi-silicates
Basic slags	Fusible	Acid Slags
Stony, melt suddenly. Very liquid Oxygen ratio 1 : 1	Slags.	Vitreous,soften gradually Oxygen ratio 1 : 2
	$3ROAl_2O_3$ Aluminous.	

The oxygen ratio of $Al_2O_3 : SiO_2$ should lie between 1 : 3 and 1 : 2. This is equivalent to saying that the limits should lie between one molecule of alumina to 4.5 molecules of silica and one molecule of alumina to 3 molecules of silica. Expressed in ordinary relations by weight the limits are: 1 part of alumina : 2.64 parts of silica and 1 part of alumina : 1.76 parts of silica.

No complete table or curves showing the melting points of slags have as yet been prepared. R. Akerman* has determined the heats of fusion of singulo-silicate slags for a series of alumina-lime ratios:

Oxygen Ratio Alumina / Lime.	0.20	0.25	0.30	0.40	0.50	0.70	0.90	1.00	1.20	1.50	2.00	2.35
Total heat of Fusion per unit Weight. Calories.	428	410	380	363	349	347	335	361	377	400	430	461

Gredt** gives the formation temperatures of singulo-silicates, $2ROSiO_2$, for a number of alumina-lime oxygen ratios:

Stahl und Eisen, 1890, p. 24.

**Jueptner's Siderology*, p 206.

Number.	Oxygen Ratio Alumina—Lime.	Temperature of Slag Formation.
1	0.00	1570°C
2	0.05	1526 "
3	0.11	1492 "
4	0.18	1468 "
5	0.25	1451 "
6	0.33	1439 "
7	0.43	1430 "
8	0.54	1422 "
9	0.67	1417 "
10	0.81	1412 "
11	1.00	1410 "
12	1.22	1430 "
13	1.50	1468 "
14	1.86	1526 "
15	2.33	1613 "

The curves on page 51 are taken from Jueptner's Siderology and illustrate the heats of fusion for various stages of acidity and lime-magnesia combinations.

In regard to the structure of slags we can distinguish glassy, stony, and crystalline slags. Silicious slags, on rapid cooling, invariably change to the glassy condition, but any slag assumes the stony appearance if cooled sufficiently slowly. Highly basic slags are always stony and frequently show fine crystals in the interior especially if ferrous iron be present in larger amounts. Silicious slags show but slight tendency to crystallize. Highly basic slags or such low in alumina on exposure to air gradually fall to a powder due to the action of carbonic acid and water. On examining strongly basic slags with the microscope Dr. Passow* found crystals very much analogous to the crystals found in Portland cement, known as alite. Certain slags possessing a peculiar tendency to fall to powder due to an inter-molecular change similar to the dusting of Portland cement were found to contain a definite mineral showing double refraction and pronounced parallel striation. Dusting Portland cement clinker was found to contain the same crystals, known as felite.

J. H. L. Vogt, of Christiania, has made the most thorough and searching examination of the crystalline structure of slags. He has succeeded in identifying a considerable number of minerals in various slags by cooling them very slowly. In the table on page 52 a number of these minerals are enumerated and their composition given together with the type of slag in which they were found:§

Stahl und Eisen, 1884, Aug. 1st.

§Jueptner's Siderology, p. 28.

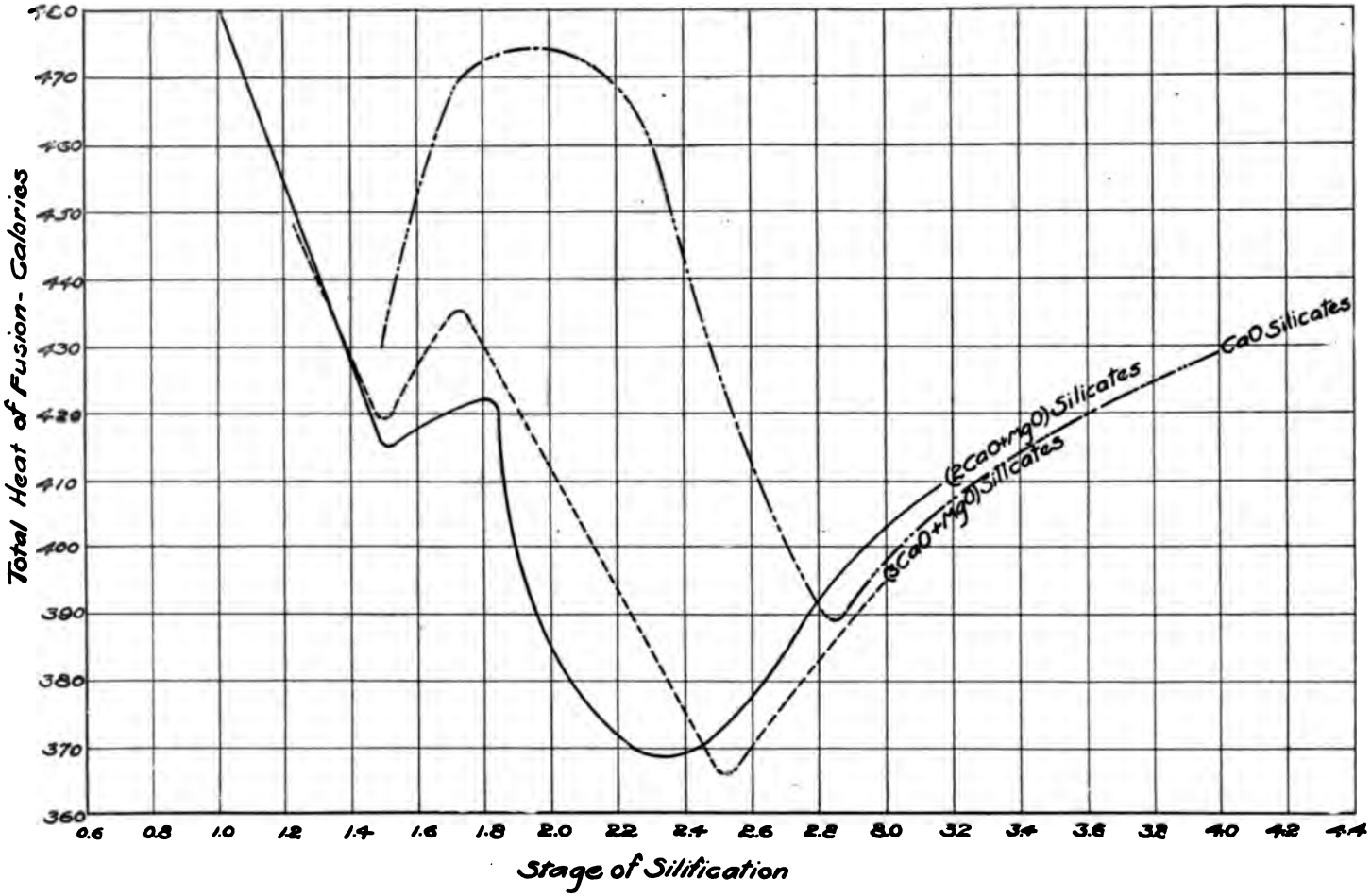

Fig. 3. Curves representing the heats of fusion of lime and lime-magnesia silicates of various acidities.

Oxygen Ratio of Slag $\frac{SiO^2}{RO}$	Typical Formula of Slag.	Minerals.
0.67	R_3SiO_5...	Gehlenite $(RO)_2Al_2O_3(SiO)_2$ Tetragonal.
1.00	R_2SiO_4...	Melilite $(RO)_{12}(Al_2O_3)_2(SiO_2)_9$ Tetragonal.
1.00	" ...	Olivine $(MgO)_2SiO_2$ Rhombic.
1.00	" ...	Fayalite $(FeO)_2SiO_2$ "
1.00	" ...	Tephroite $(MnO)_2SiO_2$ "
1.00	"	Montecellite $CaOMgOSiO_2$"
1.00	" ...	Willemite $(ZnO)_2SiO_2$ "
1.50	$R_4Si_3O_{10}$.	New, non-aluminous, calcareous, tetragonal, mineral: akermanite, $R_4Si_3O_{10}$
2.00	$RSiO_3$....	Calcium Silicate, $CaSiO_3$, hexagonal.
2.00	"	Wollastonite, $CaSiO_3$, mono symmetrical.
2.00	"	Augite varieties $CaO(Mg)SiO_3$, mono symmetrical.
2.00	"	Babingtonite $n(Mn,R)SiO_3+Fe_2Si_3O_9$, Asymetrical.
2.00	"	Enstatite, $MgSiO_3$, Rhombic.
2.00	"	Hypersthene } Fe,Mg,SiO_3, Rhombic.
2.00	"	Broncite }

In regard to the relation between the minerals and the composition of the slag, Vogt says: "A comparative examination of the analyses shows that the formation of minerals in the molten mass depends chiefly on the chemical composition of the average mass. The divergent physical conditions possible in the formation of the slags exert only a minimum secondary influence on the reaction provided a certain minimum time limit be not exceeded for the period of crystallization."

Calcined Clay.—Whenever dehydrated clay is required for pozzuolane purposes, be it for a pozzuolane cement proper or for mixture with Porltnad cement, it is of course readily obtained by calcining the clay either in a vertical shaft kiln similar to a limekiln or in a rotary cylinder furnace.

RAW MATERIALS OF THE NATURAL CEMENT INDUSTRY.

By natural cement we mean those natural, intimate mixtures of calcium carbonate and clay which when burnt to a temperature of approximately 900 to 1000° C. produce a hydraulic cement. The United States are rich in materials of this kind, and these cements have been an im-

portant factor in the development of our country during the greater part of the nineteenth century. They have been especially important during the canal-building period, during the construction of the American canal systems, the Erie canal of New York, the Pennsylvania and Ohio canals. In the construction of all these waterways hydraulic limestone was found at many places; large as well as smaller local deposits were thus discovered and used.

From what we now know of the nature of limestone we can realize without difficulty that these stones were apt to be of all sorts of compositions, high or low in clay substance. When they contain 75 to 80 per cent. of calcium carbonate and 25 to 20 per cent. of clay, they are called hydraulic limes, while those higher in clays come under the term Roman cement, containing 50 to 70 per cent. of calcium carbonate and 50 to 30 per cent. of clay. Both may contain varying amounts of magnesia. Physically, these materials may vary enormously, since they may be soft or hard, like clay in appearance, or compact as the densest varieties of stone. The harder, more rock-like hydraulic materials are preferred, since in manufacture it is desirable to work with larger lumps which are not friable, so that they may be stacked up in the kiln without impairing the draft and in order that the heat may pass through the mass uniformly.

We can, therefore, classify the natural hydraulic cements as follows:

1. Hydraulic limes..... { Calcareous. / Magnesian.

2. Roman Cement Stone.... { Calcareous. / Magnesian.

The practical distinction between the hydraulic limes and the Roman cements is that the former after burning slake by themselves and evolve considerable heat, while the latter, though quite soft, must be ground to a powder and evolve less heat of hydration on slaking. In either class the magnesium carbonate may be anything from a trace to about four-fifths of the calcium carbonate, that is, for a content of 43.5 per cent. of calcium carbonate we may have 36.5 per cent. of magnesium carbonate, the sum of the carbonates being the maximum content of carbonates allowable in a hydraulic lime.

Owing to the fact that hydraulic lime is such an extremely irregular source of cement making material, it need not be considered in detail here, but we shall discuss only the Roman cements as representing the general type of natural cements.

In the following table some typical analyses of Roman cements are given:

Number.	Percentages.							Molecular Ratio RO:SiO$_2$	Oxygen Ratio RO : Al$_2$O$_3$: SiO$_2$
	Silica.	Alumina.	Ferric Oxide.	Calcium Carbonate.	Magnesium Carbonate.	Potash.	Soda.		
1	15.65	6.80	2.50	69.00	3.40	.....	.....	2.72 : 1	2.72 : 0.76 : 2
2	16.41	5.44	3.38	46.52	26.40	.....	.....	2.85 : 1	2.85 : 0.58 : 2
3	32.06	21.27	2.11	35.56	7.00	.....	.....	0.82 : 1	0.82 : 1.17 : 2
4	23.34	8.70	1.60	38.34	23.24	.....	.....	1.70 : 1	1.70 : 0.66 : 2
5	22.73	10.43		34.54	21.85	3.63		1.59 : 1	1.59 : 0.81* : 2
6	24.30	7.22	5.06	33.70	20.94	.....	.....	1.30 : 1	1.30 : 0.51 : 2
7	22.62	7.44	1.40	40.68	22.00	2.23		1.77 : 1	1.77 : 0.57 : 2
8	24.40	6.20		41.80	16.29	1.52		1.51 : 1	1.51 : 0.45* : 2
9	27.60	10.60	0.80	33.04	7.26	7.42		0.91 : 1	0.91 : 0.68 : 2
10	28.02	10.20	8.80	44.48	1.00	0.50		1.20 : 1	1.20 : 0.64 : 2
11	22.70	7.40		36.31	25.72	.....	.....	1.77 : 1	1.77 : 0.56* : 2
12	25.16	6.33	1.71	36.08	18.38	5.27		1.38 : 1	1.38 : 0.44 : 2
13	22.91	8.00	1.90	61.76	2.70	.....	.....	1.70 : 1	1.70 : 0.62 : 2
14	24.74	16.74	6.30	41.80	8.60	6.18		1.27 : 1	1.27 : 1.19 : 2

*The Al$_2$O$_3$ includes the Fe$_2$O$_3$, the latter not having been determined.

Analysis No. 1* represents a Roman cement mined at New Lisbon, Ohio, belonging to the Lower Freeport horizon, a hard rock which produces a most excellent cement when properly burnt.

No. 2* is a similar cement rock from Bellaire, Ohio, which is mined in the hills below this city.

No. 3* is a calcareous rock found at Barnesville, Belmont county, Ohio, lying between the Pittsburg and Meigs Creek coals, Nos. 5 and 9.

No. 4 is a hydraulic shale obtained near Defiance, Ohio, highly charged with bituminous matter and containing distinct layers of pyrites which, unless removed by hand picking, interfere seriously with the proper burning of the material. The quality of cement produced from it, however, is high and it has been used in a great many buildings of Auglaize county.

No. 5 represents the Rosendale cement rock, one of the typical American Roman cements. It is chiefly found in Ulster county, New York, and is a dark blue, hard rock brought to the surface by upheavals and is hence tilted in every conceivable inclination. It is obtained by mining.

No. 6 is an average analysis of several Rosendale Roman cements.

No. 7 represents the Akron cement, of the type of the Rosendale Roman cement and mined at Akron, New York.

No. 8* is an analysis of another well-known American Roman cement, being mined and burnt within a small area along the Ohio river extending about fifteen miles north of it near Louisville, Ky., being known on the market as Louisville cement.

*Ohio Geological Survey, Vol. VI, Chapter on Cements, by Prof. N. W. Lord, p. 673.

No. 9 shows the analysis of the Utica cement, mined at Utica, Ills., the rock being a clayey limestone of Lower Silurian age.

No. 10 is a natural cement found at Round Top, Md.

No. 11 is a Roman cement manufactured near Buffalo, N. Y., of the Rosendale type.

No. 12 also is a cement of the Rosendale type, but manufactured at Milwaukee, Wis.

No. 13 represents the famous Lehigh Valley rock, mined near Allentown, Penn., in the villages of Copley, Siegfried and other places. The Roman cement made from this rock is of high quality and is also being used in the manufacture of Portland cement, limestone lower in clay being added to produce the correct composition.

No. 14 is a cement rock obtained at Cumberland, Md.

On examining the chemical composition of these hydraulic cements it is found that the average molecular ratio of $RO:SiO_2$ is 1.60:1 and that the average oxygen ratio, $RO:Al_2O_3:SiO_2$ is 1.60:0.69:2. The variations in composition, it will be noted, are very great indeed, and it seems as if the hydraulic activity were not a function of definite compounds, but is dependent on a pozzuolanic reaction which merely requires enough base to "unlock" the silica. The difference in the rate of setting of these cements is evidently governed by their content of alumina as well as of calcium oxide. Beside the chemical composition the uniformity of composition of a rock deposit, its fineness of grain and intimacy of mixture of the carbonates and the clay must be carefully considered. Coarse, crystalline limestone with irregular patches of clay would not be suitable at all, the same being true of fine grained carbonates and coarse clayey matter. On dissolving a sample of cement rock in hydrochloric acid, filtering off the residue, treating it repeatedly with hot sodium carbonate solution and finally washing out the reagents used, the residue of clayey matter can be examined. The photograph on page 56 shows the residue thus obtained from Rosendale cement, as seen under the lower power of a microscope. It was found to consist of amorphous clay substance, shown by the dull non-crystalline patches, more or less crystalline orthoclase fragments clouded around the edges by kaolinization, some flakes of mica and sharp edged crystalline fragments of quartz.

RAW MATERIALS OF THE PORTLAND CEMENT INDUSTRY.

The constituents introducing calcium oxide may be limestone, marl, slag, or industrial waste products. The clay components may be introduced as clay or mixtures of clay and sand, or as cement stone, a calcareous material high in clay base. In the great majority of Portland cement plants the mixture consists of two distinct components, the one introducing the clay, the other the necessary lime. The cement stones of the Lehigh Valley, containing more than the required clay, need the addition of a

purer limestone. So also with blast furnace slags, which are often a most excellent material for cement manufacture. Both the natural cement rock and the slags have been discussed in previous paragraphs and there remains now the discussion of the clays and calcareous material with special reference to the Ohio resources.

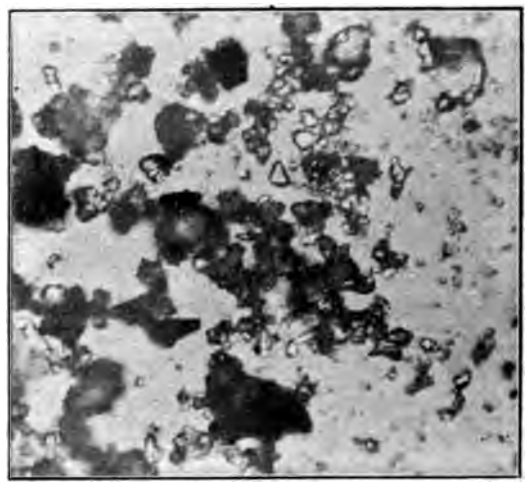

Fig. 4. Clay residue of Rosendale cement, seen under the microscope.

THE CLAYS.

Clay may be defined as a complex derivative rock, generally of a soft and earthy nature, in which a mass of mineral debris of variable composition and amount is bonded and held together by a matrix of kaolinite, or allied hydrous silicates of alumina. The distinguishing characteristics of clays as a class are, first, plasticity when mixed with the right quantity of water, and second, the property of hardening by heat, to form strong and durable silicates not easily destroyed by weather or other natural agencies. This definition is not rigidly exact, as some clays are not plastic, and others do not harden to make durable silicates by heat, but these are minor exceptions to the group as a whole.

In order to fully comprehend the nature of clay and to understand the source of its advantages and disabilities as an ingredient in cement mixtures, it is necessary to devote some space to a discussion of its origin and classification.

Origin of Clay. —As before stated, clay is a complex rock and not a single mineral. The characteristic or essential part of it, however, is the mineral kaolinite, which is derived from the weathering of feldspar and many other igneous aluminous silicate minerals.

Considering the typical feldspar, orthoclase, we find that it possesses the formula: K_2O, Al_2O_3, $6SiO_2$ and the following percentage composition:

Silica .....64.68 per cent
Alumina .....18.43 per cent
Potash .....16.89 per cent

being an alkali-alumina silicate.

Kaolin, on the other hand, has the formula Al_2O_3, $2SiO_2$, $2H_2O$ and the percentage composition:

Silica .....46.3 per cent
Alumina .....39.8 per cent
Water .....13.9 per cent

which is a hydrous aluminum silicate.

The significant changes noticed are the removal of the potash and a part of the silica and the introduction of chemical water. The obvious physical change is in the metamorphosis from a hard, crystallized substance to a material soft and plastic in character.

While the feldspar has undergone decomposition, the augite perhaps has also been attacked in a similar manner, while the mica is much slower to succumb to the destructive agencies and the quartz remains practically unchanged as far as chemical atmospheric influences go. It can be readily seen that thus the end product of the decomposition of the granite is not, in the nature of the case, a homogeneous product, but must consist of kaolinite clay substance, mixed with undecomposed fragments of feldspar, weathered and unweathered augite, mica and quartz. The material resulting from the decomposition of the augite closely resembles clay substance, but instead of being white in color it is discolored by the iron from the original mineral, resulting in a red clayey mass.

Since, however, the number and variety of aluminum silicates which on decomposition result in some modification of the clay substance is very large, it is evident that the end product must be extremely variable in composition, resulting in hydrous aluminum silicates of varying chemical and physical character, all of them being contaminated with quartz. For instance, in speaking of feldspar, the term includes both the acid feldspars, like orthoclase, albite, and oligoclase, and the basic ones, like labradorite and anorthite; the iron carrying minerals may be augite, mica, hornblende, or even magnetite, limonite and pyrites.

The character of the clay must invariably be dependent on the character of the rock from which it is derived, and since there are so many kinds of igneous rocks, granite, syenite, dolerite, trachyte, gabbro, diabase, andesite, porphyry, we see again how heterogeneous a product the primary clay materials must be. White clays are, hence, exceptional, owing to the great abundance of iron carrying minerals, and are found only under favorable circumstances and hence are comparatively valuable.

The clays so far discussed are primary clays, produced by decomposition from the original rock *in situ* without transportation of the decomposed material. Since water, that all-powerful

agent, shows its influence everywhere, especially with reference to the transportation of materials, there are comparatively few localities that escape its action. The natural result, hence, must be that the decomposed material is carried away, ground up in creeks and rivers and deposited, the coarse in rapidly moving water, the finer in still water, and the finest is carried out into the ocean or lakes to form the great deposits of shales. In this great grinding and deposition process the various portions of rock debris are mixed more or less thoroughly and can be said to possess a certain homogeneity only when deposited in deep still water, producing our fine-grained shales. All clays deposited by water are called secondary clays and comprise the vast areas of clay which we know in geology, the primary clays being more accidental in nature and small in extent. Thus the eternal cycle goes on. The igneous rocks are decomposed, worn away, carried by the streams and deposited; the beds of shale, built up slowly in this manner by movements of the earth's crust, are exposed and are again worn away to be redeposited.

The clays of this class differ from the primary clays in several respects. Owing to the fact that they have undergone transportation and mechanical abrasion they are bound to be finer grained than the first class of clays and hence plasticity, the characteristic property of clays, is much more fully developed, except, of course, when sand or similar non-plastic material is mixed with it on the way from the old rock to the place of sedimentation. The work done by the water upon the mixture of rock minerals may be placed into four functions:

1. Transportation.
2. Grinding.
3. Mixing.
4. Grading by sedimentation.

Transportation must, of course, take place if the primary rock is to be converted into a sedimentary one. The agent of transportation is always water, gathering in the mountains from small and weak streams fed by glaciers or springs. As these grow in volume and rush down into the valleys they carry with them large pieces of rock which are left behind at the foot of the mountains owing to the decrease in the velocity of the stream. With the slower current smaller particles of rock are brought along till finally near the sea the solids carried by the rivers consist of the finest particles of mud. We see thus that the size of the rock fragments transported by the water is a function of the current velocity. According to W.Hopkins,* the transporting power of water increases as the sixth power of the current velocity; thus if the velocity is doubled its motive power is increased 64 times.

But as the rocks are carried along and rubbed against the stream bottom they are continually undergoing mechanical abrasion and the

*Physical Geology, A. J. Jukes-Browne, p. 128.

amount of the finer particles is constantly increasing, which then are carried further down the stream till they either settle to the bottom, owing to the decreased stream velocity which cannot carry them any further or if fine enough till they have reached the still water of great lakes or oceans.

It is evident, of course, that all this grinding must bring about a thorough mixing of the rock products. If the mountain creeks brought down, for instance, the fine white kaolin resulting from the decomposition of feldspar together with ferrugineous minerals it is evident that the clay substance is bound to be contaminated with the iron bearing materials. We can say, therefore, that sedimentary clays are always less pure than the white clay substance arising from the original rocks under favorable conditions. The purest sedimentary clay on being burnt shows invariably a more yellow or reddish tinge than the washed primary kaolin owing to the presence of more iron. But this, though of great importance to the potter, is not of any interest to the cement manufacturer.

Since, as we have seen, the rock particles are carried along by a stream until the current velocity becomes too small when they settle to the bottom, we can also say that the greater the velocity of the current the larger will be the size of the particles deposited by it. The more rapid the flow of the river the coarser will be the sediment on its bottom. Very fine clay materials will hence be deposited only in oceans or lakes where the water is still. But since the velocity of a river varies we find that sometimes coarse materials alternate with fine; even at the same point in a river coarser material may be deposited in the middle of the stream while in a bend or pool, the water being comparatively quiet, fine clay settles out. We cannot, therefore, expect to find uniform deposits of clay formed by smaller rivers and creeks, but must look for them in beds of large rivers, lakes and oceans.

Water deposition not only grades materials according to their size, but also according to their specific gravity. This is due, of course, to the fact that heavy particles settle first, followed by the other materials in proportion to their specific gravity. Similar particles of the same kind will hence be deposited together in horizontal layers. We must keep in mind this grading process of nature in order to understand why shales deposited in still water are so uniform in character, or why alluvial clays have such a varying composition.

Alterative Influences to Which Clays are Subject.—We can readily see how clays may be deposited under various conditions. If the stream has carried along clay together with very fine ground quartz the resulting deposit will be a silicious clay, if with ground calcite or limestone we shall have a calcareous clay, or if with organic matter bitumin-

ous or graphitic material. But even after decomposition the clays are subject to various changes, due to the chemical and physical conditions to which they may be exposed and geological disturbances which may arise. These changes are often very complicated, acting upon the clays simultaneously and reacting also upon each other. But in order that we may have a proper conception of the changes possible, we must consider each of the various influences and study the effect wrought by it upon the clays. It is evident, of course, that each of these actions has a different effect on different clays.

The influence to which clays may be subjected may be grouped together as follows:

1. Wearing away and redeposition.
2. Metamorphism due to { heat, pressure, steam and other gases.
3. Chemical action.
4. Solution and crystallization.
5. Infiltration.
6. Leaching.
7. Concretionary action.
8. Glacial action.

Wearing Away and Redeposition.—No material is able to withstand the attacks of the great weathering agents, water and air, assisted by the physical factors, heat and cold, and durability is hence only a relative term of no significance geologically. As soon as a clay is deposited it is again subject to changes, more or less radical. It is worn away and transported by water, either to be redeposited as clay or to become part of another rock. If the clay happens to be pure it is liable to be rendered impure by this process, if already impure it stands some chance of being purified by the removal of coarse constituents, sand, organic matter, concretions, etc. Such is the case with certain glacial clays where a heterogeneous jumble of materials is worn away and redeposited free from all coarse mineral matter. This is the case in certain localities of northern Ohio, as at Milbury, where a glacial clay was by this process redeposited as a fine grained material in a fresh water lake and was thus freed from the rock debris peculiar to bowlder clays.

Metamorphism.—In the mountain-forming periods of the earth's crust, when the rock strata underwent crushing and crumbling, both heat and pressure were brought to bear upon the rocks, changing their structure and character. Similar metamorphosis is experienced by the strata when coming in contact with fused masses of lava, where heat brings about the alteration. In this manner shale is readily transformed

into slate or the clays may even be brought to the condition of an igneous rock as soon as the heat is sufficient to melt them.

Steam especially in the superheated condition is a powerful agent in the decomposition of all silicates. This may readily be shown experimentally, when it will be found that even very acid silicates are decomposed without trouble. When in Germany extensive attempts were made by Professor Meyer to burn lime at a lower temperature by means of superheated steam so as to produce a better product for the purposes of the sugar industry these were eminently successful as far as the lime burning was concerned, but had to be given up because the kiln linings of fire brick and the iron pipes were destroyed so rapidly. We can readily see that clays in contact with superheated steam will be completely decomposed and their entire character destroyed. Similarly, the action of volcanic gases like carbon dioxide, hydrogen sulphide, etc., is bound to result in a material alteration.

Chemical Action.—The chemical changes which clays undergo represent a continuous chain of reactions which never cease. Though the chemical processes constantly taking place are infinitely numerous, we may distinguish principally two kinds of reactions, namely, oxidation and reduction. It is evident that these reactions involve principally those compounds which are easily oxidized and reduced, especially the oxides of iron and manganese, though the latter is present in clays in such small quantities that it may be neglected. If a clay happens to contain its iron in the state of the lower oxide, as the carbonate, or as the sulphide, FeS_2 (iron pyrites) the atmospheric oxygen brought in by water percolating through the deposit will convert it to ferric oxide or its equivalent, ferric hydroxide, or the sulphate. The whole character of the clay is thus changed, which is usually shown by the difference in color. A bank of shale, for instance, near the surface will possess a reddish or yellow color owing to the presence of the higher oxide of iron, while on working into it the color is found to be blue or gray, indicating ferrous iron. At the same time the surface shale will be found to be soft and easily worked while that in the hill is hard and rock-like.

Conversely, if an oxidized clay is exposed to reducing conditions resulting from organic matter the iron is changed to the ferrous condition, producing ferrous oxide and ferrous carbonate from the ferric oxide and ferrous sulphide from the sulphate. Hydrogen sulphide would naturally convert the iron to the sulphide.

There are a great many other possible reactions, such as the decomposition of ferrous or ferric sulphate and calcium carbonate resulting in the production of the ferrous or ferric hydroxide or oxide and calcium sulphate, carbon dioxide being evolved. Similarly, magnesium sulphate may be produced from the iron sulphides and sulphates as we know it to

enter the water from coal mines. Even free sulphuric acid may be produced under favorable conditions. Hydrous silicic acid brought into a clay may be precipitated by calcium carbonate and iron compounds by the action of organic acids.

All these reactions are coincident with the processes of solution, infiltration and crystallization.

If the tendency of the chemical reaction is to make the basic constituents of a clay more soluble they are taken up by water, dissolved and carried somewhere else and allowed to crystallize there. A clay may thus become purified while at the same time another material is being charged with the elements removed.

Solution and Recrystallization.—The matter of solution and crystallization has already been touched upon. Practical examples of this kind of action are quite frequent. In a shale, high in sulphur compounds, these become oxidized and soluble in water and are removed by the water to a lower point where crystallization takes place. If from the ferrous sulphate calcium sulphate is produced the latter will crystallize out as gypsum. The gypsum crystals thus produced may be frequently found in the soft clay at the outcrop of a shale deposit. Crystallization is not restricted to this one kind of substance, but may involve all of the soluble constituents and even may be observed in the clay itself where frequently the outlines of large crystals may be traced.

The crystallization of soluble constituents in a clay often condemn it for building purposes since these salts give rise to the unsightly efflorescence called "white wash" in the wall.

Infiltration.—We have already seen how soluble constituents may be dissolved and taken away to another part of a clay bed. These soluble constituents may, of course, come also from another rock and may be precipitated in the clay. Thus, soluble silicic acid brought in by deep seated springs is readily precipitated in the clay by calcium carbonate, iron salts by various organic compounds. As a result we would find veins or streaks of the materials introduced by infiltration wherever the water flowed, as we frequently find clays showing iron stain in an irregular network.

Leaching.—Wherever an impure but uniform deposit of clay is subjected to the action of organic acids and at the same time an outlet for the materials dissolved is provided it is bound to be purified by this leaching action. All of the soluble and also ordinarily insoluble compounds are made soluble and removed by the organic compounds. In time there will be left nothing but a mass closely resembling pure clay substance and whatever quartz was originally contained in the clay. Many of our Ohio fire clays have been produced in just this manner.

Concretionary Action.—Concretionary action is often active in collecting materials like ferrous carbonate or calcium carbonate in the clay and

causing it to form balls or pebbles of various sizes. Such concretions are met frequently and of course cause the clays to be irregular in composition. If they occur in too great a quantity they may render the clay worthless. Often, however, they may be removed by hand picking.

Glaciation.—By glacial action we mean in general the effect wrought upon rock material by the movement of ice upon it and the admixture with the rock debris brought along by the ice. This action may, of course, be more or less pronounced. It may remove the original clay, entirely, replacing it by the glacial drift material, as we know it to have taken place in large areas of Ohio where for instance the black shale has disappeared entirely, or it may produce a heterogenous mass of clay containing bowlders of igneous rock and fragments from both igneous and sedimentary rocks. In any case extreme irregularity of composition will be produced and what might originally have been a good clay is now utterly unfit for the purposes of the cement industry. Unless such clays are worn away and redeposited there is little encouragement for their practical utilization.

Composition of Clays.—We have thus seen that in adding clay to a Portland cement mixture, we are adding a complex mixture of minerals, each of which has its own characteristic behavior in the vitrification process to which the cement is subjected. While no two clays are ever exactly alike, and while the fluctuations in composition and properties of clays may be very wide, it is still possible to make some general statements concerning them. They are known to be composed chiefly of four kinds of mineral matter. These elementary minerals, of which three are silicates and the fourth is wholly silica, are

Kaolinite or clay substance.
Feldspar and the feldspathic minerals.
Mica and the micaceous minerals.
Quartz or crystallized silicas.

These, blended in every conceivable proportion, form the predominating part of clays; in addition, there are frequently considerable quantities of ferruginous, calcareous, or carbonaceous matter, which may be in quantity sufficient to dominate and give character to the rock as a whole. Small quantities of other minerals are always present, but these are not factors of importance in the cement industry.

The behavior of a clay in a Portland cement mixture will, therefore, be the resultant of the behavior of its component minerals, which will now be studied.

Behavior of Kaolinite.—The importance of the clay substance in cement-making becomes manifest when we study its behavior with calcium carbonate or limestone on heating, and compare it with ground quartz. While fine quartz, ground in a ball-mill, on being heated with pure, fine cal-

cium carbonate only had 71.17 per cent. of silica rendered soluble in hydrochloric acid and sodium carbonate solution, clay substance in the shape of washed kaolin, on being treated exactly like the quartz, was practically all taken into solution. Again, if we heat kaolin and calcium carbonate together we find that the reaction between these two substances takes place at a much lower temperature than between very fine quartz dust or even silica prepared by precipitation from a sodium silicate solution. The expulsion of the combined water from the clay substance is soon followed by, or to some extent is even coincident with, the evolution of carbon dioxide from the calcium carbonate, so that at about 900° C. the clay substance, having lost the chemical water, has the latter replaced by calcium oxide, and in place of Al_2O_3, $2SiO_2$, $2H_2O$ we have $Al_2O_3 2(CaOSiO_2)$.

Prof. Lunge and Dr. Schochor, two German investigators, showed ten years ago how much more available the combined silica of the clay substance is than even the amorphous silica obtained by precipitation.

Practical experience in cement making demonstrates clearly that the more "clay" a material contains, the more readily does it vitrify a cement mixture, that is, the lower a temperature is required.

It seems thus that combined silica in the shape of clay substance is the most efficient source of silica for the production of the lime silicates required in cement-making, viewing the subject from the chemical standpoint.

If pure kaolin were used for a cement mixture, there would be introduced, of course, a certain amount of alumina; for every part of silica we would have 0.86 part of alumina, the ratio of silica to alumina being 46.3 : 39.8=1.16 to 1.00. Without going further at present, let it suffice to say that this brings in too much alumina and hence the problem of introducing readily available silica for the union with the lime cannot be solved by the simple expedient of using a pure clay, high in clay substance. Though as much silica as possible should be brought in as combined silica, the alumina content must be kept within the bounds prescribed by experience, and the balance of the silica must be introduced as free silica or quartz. It should be as fine as possible, so that nature's grinding process is utilized, saving the expense of artificial grinding. In some text-books, it is prescribed that a clay for cement-making should contain no free silica and that its alumina content should be about one-fourth of the silica content. This evidently is an absurdity, as for every part of silica the clay substance contains 0.86 part of alumina.

Feldspar.—The second constitutent almost invariably present in clays is feldspar, in the shape of more or less decomposed fragments, still remaining from the incomplete decomposition of the original rock or brought in from other rocks by way of water transportation. The particles, according to the degree of grinding which they have undergone, are coarser or finer, like the particles of sand. As a rule they are finer than the

quartz, being less resistant to mechanical abrasion, but coarser than the clay substance. The term feldspar used in this connection is not strictly accurate, since there are a number of feldspathic minerals having various compositions. Yet since one kind of feldspar, the orthoclase, predominates so largely, the error for all practical purposes is not great enough to affect the technical results. In speaking of feldspathic matter we, therefore, mean orthoclase. In some clays, oligoclase is more abundant than the orthoclase, but anorthite is as a rule insignificant in amount.

The following table of chemical compositions will show the difference in the constitution of four feldspars:

Name.	Chemical Formula.	Percentage Composition.					Percentage Ratio of Silica to Alumnia.
		Silica.	Alumina.	Potash.	Soda.	Calcium Oxide.	
Orthoclase.	$K_2O\ Al_2O_3\ 6SiO_2$..	64.70	18.4	16.9	.....	.....	3.52 : 1
Albite.....	$Na_2O\ Al_2O_3\ 6SiO_2$	68.70	19.5	.....	11.8	.....	3.55 : 1
Oligoclase..	$Na_2O\ CaO\ 4.5\ SiO_2$	63.00	24.0	.....	10.0	3.0	2.63 : 1
Anorthite..	$CaO\ Al_2O_3\ 2SiO_2$..	43.20	36.7	.....	.....	20.1	1.18 : 1

The Function of Feldspar in Cement.—Feldspar, like kaolinite, is a silicate, it being a double silicate of alumina and alkali. The silica, being in the combined state, is readily available for the purposes of cement-making, and hence we find that on heating it easily combines with the lime. The difference between clay substance and feldspar in this respect is not great. Clay substance is more readily decomposed by lime on heating, but this is to some extent due to the extreme fineness of its particles and their shape, which makes them especially ready to come into intimate contact with the lime particles. Feldspar is hence an admirable source of silica. The alkali, being a powerful flux, causes the clay containing feldspar to become less refractory. While clay substance is an ideal refractory material, fusing at a temperature above the melting point of platinum, approximately at 1830° C., feldspar melts at about 1290° C. Hence any content of feldspar in clay is bound to reduce the melting point of the latter unless it has already been lowered below the melting point of feldspar by means of other fluxes, like iron, lime, magnesia, free alkalies, etc.

We can therefore say that feldspar in clay which is used for making cement reduces the temperature of combination with lime, first on account of its initial greater fusibility; second, because of its readily available silica. We can say, hence, that it is a desirable constituent of clay, and the more so because it brings in a comparatively small amount of alumina, one part of silica introducing only 0.284 part of alumina.

Some writers object to the presence of the alkalies, potash and soda brought in by the feldspar, claiming that it does not lower the temperature of combination (or clinkering) and hence is useless; also that it causes the cement to set too rapidly, and again that the free alkalies resulting from the decomposition of the feldspar by the lime are liable to cause injurious efflorescence.

The writer in his experiments has found that these claims are exaggerated. The clinkering temperature was reduced by the addition of even small amounts of feldspar and the cements produced were of normal setting qualities.

Micaceous Minerals.—These are found in all clays, owing to the fact that mica is a mineral resisting atmospheric influences extremely well, due to its parallel cleavage. Since the shape of the particles as flakes causes them to float readily, we find them invariably associated with clay substance, from which they cannot be removed by any washing process. But as a rule the amount of micaceous minerals present is not great, though they are never absent.

The principal mica is muscovite, $K_2O3Al_2O_36SiO_22H_2O$, which we find has a strong similarity in composition to feldspar (orthoclase), since it contains only two more molecules of alumina than feldspar. We might say therefore that it is a somewhat weaker flux than orthoclase. In regard to the availability of the combined silica, of course, there can be no difference.

The fusibility of mica has been compared with that of feldspar, both being ground very finely and incorporated in a clay body.* It was found that 2.308 chemical equivalents of mica exert the same fluxing power as one equivalent of feldspar, other things being equal. This fluxing ratio is probably still lower for clays which have not undergone extremely fine grinding by the wet process, as the flakes of mica are very difficult to reduce to impalpable powder, and in the shape of flakes the mineral has no appreciable fluxing influence upon the clay mixture.

From the chemical standpoint we can safely say that for all practical purposes mica may be collected under the heading of feldspathic minerals, especially since the amount present is but small, so that really the only difference between a feldspathic and a micaceous clay would be a somewhat higher fusing point. By adopting this assumption the analytical work of separating the minerals of a clay is simplified considerably. As has already been said, the bulk of the mica is decomposed as readily by the action of the calcium oxide at higher temperatures as the feldspar, but the reaction is governed much more by the amount of grinding the mica has undergone, that is, by the size of the flakes, as the structure makes fine disintegration very difficult.

The Quartz in Clays.—The behavior of quartz in cement mixtures has been discussed partly in other connections. It is found in clays in grains

*R. T. Stull, "The Fluxing Power of Mica in Ceramic Bodies," Transactions American Ceramic Society, Vol. IV, page 225.

of all sizes and the particles may be worn by the natural grinding process more or less or not at all. Since we know that it should be as fine as possible so as to render it fit for the cement reaction without the expense of grinding, we should select such clays as have been ground fine by natural processes and have been washed out and redeposited in still water. Such clays are the shales and the glacial clays of the lake regions of New York, Indiana, Wisconsin and Ohio, as, for instance, the Albany slip clay of New York and the lacustral clay of Millbury and Bryan in Ohio. Geology thus aids us in finding and investigating suitable clay materials and determines whether a proper material can be furnished by a certain locality or not.

The Rational Analysis of Clays.—In speaking of clays in general we mean, according to what has been already said, natural mixtures of three mineral groups:

Clay substance.
Feldspathic minerals.
Quartz.

It must be, therefore, of interest to know just what proportion of a clay is clay substance and what free silica or feldspathic minerals. This is best determined by a chemical method, depending on the fact that clay substance is soluble in hot concentrated sulphuric acid and hot sodium carbonate solution, while both feldspar and quartz are not. By such a treatment all of the clay substance is removed, leaving only the quartz and feldspathic minerals. On analyzing this residue the amount of alumina and ferric oxide shows the percentage of feldspar present, since quartz can be assumed to consist of pure silica. Knowing the amount of the alumina and ferric oxide, the silica belonging to the feldspar is readily calculated, since the ratio between the R_2O_3 compounds in orthoclase feldspar and the silica is as 1:3.52, that is, for every per cent. of alumina plus ferric oxide, we have 3.52 times this amount of silica. The total amount of silica in the insoluble residue minus the calculated amount of silica belonging to the feldspar will give the amount of quartz and the total amount of feldspar is found by adding the silica (calculated) to the alumina and ferric oxide, the calcium and magnesium oxides and the alkalies all found in the insoluble residue. The details of this method will be given later under its proper heading.

Though this method of mineral analysis can lay no claim to scientific accuracy, it is of great practical value in giving a picture of the mineral structure of a clay which is of much greater direct benefit than the mere gross analysis.

Other Silicates.—Other natural silicates than those composing the clays have so far found no general application in the manufacture of Portland cement, but for certain purposes the use of certain silicious rocks low in iron is not an impossibility; for instance, for the manufacture of

white or very light-colored cement. Such rocks would be the pegmatites, similar to Cornish stone, used so extensively in the pottery industry; besides being low in iron, they are also low in alumina and high in silica, which would produce, if properly made, a safe cement, slow-setting, without the use of plaster. This question deserves more practical attention than it has yet received.

Classification of Clays.—It will not be found advisable to attempt a classification going into all the variations of clayey materials; for the purpose of the cement manufacture a less complicated system will suffice.

- A. Primary Clays.....
  - White or light colored rock-aggregate. Kaolins.
  - Ferruginous hydrous rock-aggregate.
- B. Sedimentary Clays
  - Fire clays....
    - Plastic kaolin
    - Flint clays.
    - } High grade clays.
    - Low grade fire clays.
  - Shales.....
    - Aluminous.
    - Ferruginous.
    - Silicious.
    - Calcareous.
    - Carboniferous.
  - Plastic Ferruginous or Calcareous clays
    - Weathered shale
    - Alluvial.....
      - Deposited in swift running water
      - Deposited in slow running water
      - Deposited in still water.
    - Glacial.....
      - Drift clay proper.
      - Re-deposited glacial clay.

1. Light Colored Rock Aggregate.—When igneous rocks of the granitic type break down under the influence of the weathering agencies, the transition from the feldspathic minerals and other aluminum silicates to hydrous kaolinitic substances is not sudden, but gradual. On top of a decomposing layer of granite we would have the finest grained clayey material, while on approaching the mother rock the rock found would bear more and more the character of the granite. Fragments of the old rock would be found surrounded by the more or less completely hydrated material.

If conditions happen to be such that the clay (kaolin) is obtained solely from the feldspathic rocks without admixture of augitic minerals or hornblende, the resulting material will be composed of clay substance ($Al_2O_32SiO_22H_2O$), more or less decomposed grains and fragments of

feldspar and grains of quartz. For the purposes of the cement manufacturer neither the pure clay substance nor the quartz are of any direct value, as the one brings in too much alumina to be suitable for cement making, while the other is too hard to be ground profitably on a large scale. Hence if the primary rocks are to be considered at all they must either be high in feldspar or high in very fine quartz. The latter is not all probable, as the primary rocks have not gone through a natural grinding process, and hence only the first case deserves consideration.

Feldspathic white clays may be used in the manufacture of white Portland cements, furnishing as they do the silica in the combined state and since they also introduce a powerful flux in the shape of the alkalies. Rocks of this type may even be considered commercially if they should happen to contain a small amount of coarse quartz. If the feldspathic minerals are fine grained while the quartz is coarse, the latter can easily be removed by washing, as is done in the preparation of the kaolins for the market. If the difference in size between the particles of feldspar and those of quartz is not sufficiently great to separate them, since their specific gravities are very nearly alike, it would probably pay to grind these materials to the required fineness. This is due to the fact that white or very light colored cements sell at a much higher price, being especially suitable for decorative construction purposes. The white clay found at Mt. Holly, Pa., is an example of the kind of material under discussion.

2. Ferruginous Rock Aggregate.—If on the decomposition of the granitic rock the iron carrying minerals, like augite and hornblende, are in part or completely broken down and these hydrous aluminum silicates are mingled with those from the feldspar and perhaps magnetite is present also, the aggregate of these decomposition products may or may not be suitable for cement making purposes. Its suitability depends first on the softness of the decomposed minerals, the character and amount of quartz present, the content of iron, the amount of clay substance, the amount of undecomposed minerals and the uniformity of the clay bed. It is not often that a material of this character will be found satisfactory; in the majority of cases it would be too heterogeneous to be of any practical value for the purposes of the cement industry.

This statement applies to all primary deposits. Since no primary clays are found in Ohio a further discussion of them will be unnecessary.

3. Fire Clays.—This is a somewhat indefinite term, standing in general for clays which do not melt at high temperatures. A great deal of confusion prevails in regard to the conception of high temperatures among practical men. Though no definite limit has ever been put down, it may be said that no clay can be called a fire clay or refractory clay unless it stands a temperature approximately 3000° F. or 1650° C., expressed in the scale of fusible cones adopted by Seger as No. 26.

These clays may be white or yellowish in color when burnt; a clay burning almost a red color may be a fire clay, but the chances are against it. The value of a fire clay can, however, be determined definitely only by a refractory test.

The high fire-resisting quality of a clay is due, first, to the absence of fluxes which either were never present in the material or which have been leached out and removed, and, secondly, the fact that it corresponds more or less closely to the composition of the ideal clay substance, $Al_2O_32SiO_22H_2O$, containing, as we know,

46.3 per cent. silica.
39.8 per cent. alumina,
13.9 per cent. chemically combined water.

The highest refractoriness is represented by a material of this compositon, as many tests have shown. We can readily see, however, that any fluxes present will deterioriate the refractoriness. But it has also been proven by most extensive experiments that silica above that entering into the composition of clay substance will act similarly to a flux and reduce the refractoriness. A clay high in silica cannot, therefore, be a high-grade fire clay. On the market a fire clay is occasionally offered as being high in silica, a fact which the dealer supposes to be advantageous, but which really classifies the clay at once as of low grade.

This important law has been put to the test both theoretically and practically, but we must keep in mind distinctly that it applies only to clays already possessing a certain degree of refractoriness. Clays high in fluxes having a low fusibility intrinsically do not come under this law; clays of this kind are raised in the refractory scale by large additions of silica.

For cement making purposes the fire clays do not come into practical consideration excepting as furnishing the material for the kiln lining. This is due to the fact that, first, these clays are very high in alumina and consequently would produce dangerous quick setting cements unfit for use; secondly, the initial refractoriness of these materials is so high that it would increase the cost of manufacture unnecessarily. Though theoretically it is possible to manufacture a cement from limestone, fire clay and sandstone, practically it is not a feasible proposition. For this reason we shall not consider the highly refractory materials in detail.

In speaking of fire clays we must distinguish principally two kinds, the plastic and the hard, slightly plastic variety.

We have in Ohio no plastic fire clays of very high quality, but we have a number of them which are of sufficiently high grade to be used for good fire brick and other refractory wares. An example of this kind of clay is the Ballou fire clay from Muskingum county, which shows the following analysis:*

*Vol. VII, Part I, *Ohio Geological Survey*, p. 222.

	Per Cents.
Silica	59.43
Titanic acid	0.95
Alumina	26.76
Ferric Oxide	1.23
Lime	0.60
Magnesia	0.32
Potash	1.00
Soda	Trace.
Combined water	10.07

The hard fire clays, the so-called flint clays of Ohio, are of much greater purity than our plastic fire clays. They closely approach kaolin in composition.

The following analysis represents a typical Ohio flint clay, from Scioto County:*

	Per Cents.
Silica	44.60
Alumina	40.05
Ferric oxide	0.80
Lime	0.27
Potash	....
Soda	....
Chemical water	14.23

Physically flint clays are hard, conchoidal in fracture and when moistened with water show but slight plasticity. On being exposed to the atmosphere they break up into sharp fragments and after longer periods of storing the plasticity is increased, but the clay never becomes sufficiently plastic to be molded with ease.

Second Grade or Number 2 Fire Clays and Stoneware Clays.—Beside the clay materials representing the highest grades of refractoriness we have a great number of clays in Ohio which are much less refractory, being higher in fluxes and free silica.

These clays associated with the coal measures of Ohio are the result of the leaching process already mentioned, by means of which the fluxing impurities have been removed more or less completely by organic agencies.

These clays are found in great variety of composition, as will be shown by the accompanying table of analyses. The main characteristics of the number two fire clays are, first, the ease with which they vitrify, which makes them particularly suitable for the manufacture of stoneware, though vitrification takes place very slowly and gradually; second, their fire resisting property, which corresponds approximately to the melting point of the Seger cone number 16, 1450° C., and third, the light buff color to which they burn. These clays are apt to contain concretionary iron sulphide in considerable quantities, which causes considerable difficulty and irregularity in the behavior of the materials on firing.

The following table† of analyses will show the chemical characteristics of these clays:

*Vol. VII, part I, *Ohio Geological Survey*, p. 220.

†*Prof. Edward Orton, Jr., Geology of Ohio*, Vol. VII, Part I. p. 94.

Number.	Per Cents of Ingredients.											Molecular Ratio Silica : Alumina.
	Silica.	Alumina.	Titanic Acid.	Ferric Oxide.	Lime.	Magnesia.	Potash.	Soda.	Combined Water.	Moisture.		
1	69.33	19.08	0.20	1.26	0.60	0.63	2.14	0.02	5.57	0 94	3 62	6 18 : 1
2	69.79	19.31	.....	.....	.....	.....	.....	.....	5.08	1.02	3 04	6 15 : 1
3	64.26	22.95	.....	1.28	0.45	0.37	1.81	0 15	6.74	2 05	2 80	4 76 : 1
4	65.20	23.05	0.55	0.99	0.58	0.58	1.45	.....	7 30	1.11	2 83	4 81 : 1
5	68.13	20.80	.....	1.20	0.42	0.37	2.28	0 27	5 72	1 00	3.27	5 56 : 1
6	56.44	26.60	.....	2.00	0.47	0.63	3 20	0.26	7.57	2 48	2 12	3.61 : 1
7	67.85	21.77	.....	1.06	trace	trace	1.93	1.11	6.07	.....	3.11	5 31 : 1
8	63.45	23.04	.....	2.03	0.72	1.03	0.53	0 93	7.81	$SO_3$0.24	2 75	4.08 : 1
9	58.86	27.96	.....	1.40	0.51	0.64	2.75		8.82	.....	2 10	3 58 : 1
10	62.81	21.41	1.26	2.65	0.58	0.85	2.80	0.21	6.52	1.47	2.93	5 00 : 1
11	70.00	19.35	.....	1.94	0.15	0.24	2.25	.....	8.35	.....	3.61	6 01 : 1
12	77.65	12.78	.....	3.32	0.55	0.45	1.30	.....	4 10	.....	6 07	10 30 : 1
13	71.58	18.31	.....	1.09	0.40	0.62	2.96		5.95	.....	3 91	6.65 : 1
14	60.50	25.53	0.54	1.66	0.38	1.19	1.76		7.98	.....	2 36	4.03 : 1

No. 1. Brumage's stoneware clay, Roseville, Ohio.
No. 2. Walker's clay, Roseville.
No. 3. Zanesville Stoneware Co.
No. 4. Uniontown stoneware clay.
No. 5. Akron stoneware clay, average of several samples.
No. 6. Salineville.
No. 7. Canton stoneware clay.
No. 8. No. 2 fireclay, Logan (analysis by L. E. Barringer.)
No. 9. No. 2 fireclay, Union Furnace.
No. 10. Island Siding clay, Jefferson Co., No. 2 fireclay.
No. 11. Toronto sewer pipe clay, top.
No. 12. Elliottsville, No. 2 fireclay, used in making sewer pipe.
No. 13. Typical stoneware clay (Langenbeck, Chemistry of Pottery, p. 80.)
No. 14. Typical No. 2 fireclay, used in making yellow ware, same author.

The mineral compositon of typical Ohio clays of this character is represented by the following analyses:*

	Clay Substance.	Quartz.	Feldspathic Detritus.
No. 13.....	53.42	44.41	3.08
No. 14.....	76.05	19.54	4.28

The extreme limits of the contents of clay substance are about 40 to 80 per cent. It is interesting to note the compositions of the clay substance which are:

	Per Cents.	
	No. 13.	No. 14.
Silica.....	47.70	50.19
Alumina.....	33.47	32.87
Ferric oxide.....	1.96	1.84
Titanic acid.....	.....	0.71
Lime.....	0.31	0.16
Magnesia.....	0.97	1.47
Alkalies.....	4.36	1.82
Combined water.....	11.13	10.50

Any of these usually very fine grained clays, with a percentage silica-alumina ratio of more than 3, can be made suitable for cement purposes by the addition of a little soft iron ore, say 1 to 2 per cent. The average percentage silica-alumina ratio is 3.22, while the average molecular silica-alumina ratio is 5.47. The latter ratios, being larger, are better for pointing out the differences. A molecular ratio of 5.1 might be accepted as suitable. But their use should be resorted to only when ferruginous clays sufficiently high in silica and sufficiently fine of grain are not available, owing to the fact that iron oxide lowers the vitrification point of cements considerably and hence stands for a lower fuel consumption. If, however, a manufacturer should be confronted by a choice between an irregular ferruginous clay deposit and a bed of silicious second grade fire clay, he would do much better to select the refractory clay, first, because it is apt to be much more uniform in composition and, second,

*Langenbeck, *Chemistry of Pottery*, pp. 67 and 80. Analyses by W. L. Evans, M. Sc.

because as a rule these clays are finer grained. Such a clay is the Roseville stoneware clay in which the percentage silica alumina ratio is 3.63:1. The magnesia in most of these clays is low and the only possible detrimental constituent to be considered would be the concretionary iron sulphide, which is injurious both on account of its irregular distribution and the sulphur it introduces.

Physically, these clays are rocky and hard when mined, but after being exposed to the weather for a short time they slake and crumble down. Their plasticity is developed only by grinding and working.

The principal geological horizons furnishing these clays are the Lower Mercer, Upper Mercer, Brookville and Lower and Middle Kittanning. Especially prominent is also the horizon of the Putnam Hill limestone.

Shales.—Geologically, we speak of shales as being, as a rule, fine grained clays, deposited in still water and later subjected to pressure, thus giving them the characteristic cleavage and structure. If this is carried further the shale becomes slate, and if another agent, heat, is introduced the metamorphism may be carried still further and the clay reverts to an igneous rock. The term shale thus stands as a guarantee, so to speak, of fineness of grain and also uniformity of composition, but does not specify the chemical composition. We may have shales high or low in refractory power, high or low in fluxes, though each is tolerably uniform within a reasonable area. We must hence keep in mind that the term shale stands for no specific chemical composition, but has only a geological meaning.

Aluminous Shales.—There is no reason why fire clays should not assume a shale structure. The most refractory clay known is a shale, the Rackonitz shale clay. Ohio has buff burning clays with shale structure which in composition correspond about to the number two fire clays, some of them being reported from near Logan. But what has been said concerning the fire clays applies also here and we may dismiss this class of clays as being too high in alumina.

Ferruginous Shales.—Shales high in ferric oxide are plentiful in Ohio and may give rise to a valuable source of cement material. The chief advantage of shales is, as we know, the great fineness of grain and uniformity of composition, but it has as its great practical disadvantage the fact that in the unaltered condition within the hills, it is hard and rather difficult to reduce to a powder, though shales may differ considerably in this respect, some being easier to reduce than others. But nature in many localities has solved this problem by causing the shale structure to become softened, giving rise to the so-called "rotten" shale which has all the good qualities of a shale, but not its hardness. Examples of this may be noticed along the outcrop of most shales, and on the surface of surface beds. The question whether such softened shale becomes available for manufacture must be determined by the amount of such material at hand. If a clay property covers a large area or if the

softened shale extends to some considerable depth, say 8 to 10 feet, the best policy will invariably be to work only the softened portion of shale along the surface, neglecting the hard main body of the shale entirely. Such a shale has usually a greenish or reddish color and is so soft that it can be readily cut with a knife, like soapstone. A material of this kind is to be greatly preferred to an alluvial deposit of clay liable to all the caprices of sedimentation by flowing water.

The color of unweathered ferruginous shale varies from dark gray and bluish gray, while the softened weathered shale assumes reddish and greenish shades.

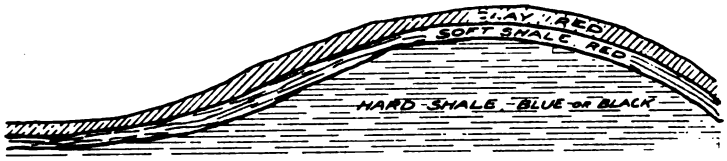

Fig. 5. Section showing the graduation of the hard shale in the interior of a hill to the soft layers on the surface.

On examining a hill of such shale (see figure 5) we find, first nearest to the surface a red clay containing fragments of shale followed by softened shale. The hard shale contains the iron usually as the ferrous carbonate and at the same time it may contain concretions, often to the size of a man's head, of ferrous carbonate, which of course are rejected. These "kidneys" of iron carbonate, if present in large quantities and in smaller lumps so that they cannot be removed by hand or machinery, cause the shale to become worthless for all manufacturing purposes. Another impurity liable to be found is iron sulphide (pyrites) in the hard shale which in the oxidized, softened shale becomes iron sulphate.

The ferrous carbonate of the hard shale becomes oxidized in the softened shale to the ferric oxide or hydroxide which gives to the shale its reddish appearance. Comparatively few shales contain iron solely as ferric oxide, one of the exceptions being the Bedford shale, a material much valued in the manufacture of front brick owing to the magnificent red color it assumes on burning.

As to the influence of the high content of iron in these shales on the cement to be produced, it may be said that as long as the content of iron does not run too high, say more than 10 per cent. of ferric oxide, the shales are to be preferred to clays lower in iron but higher in alumina, inasmuch as they cause the burning to take place at a much lower temperature and reduce the danger of spoiling the mixture in the burning by "dusting." The only possible objection which can be brought against a cement made from ferruginous shale is the darker color, which, of course, is due to the high iron content.

We may say, therefore, that ferruginous shales, provided they are sufficiently low in alumina and magnesia, do not contain too much concretionary iron and are not too hard, are well suited as cement materials. The limit of the ferric oxide content may be placed at 10 per cent.

In the consideration of these shales we must not overlook the fact that if they are too hard they are not the most suitable material, and in such a case one should try to find an area containing some of the weathered shale. The hard shale should be selected only if neither the clay produced from the shale by completed weathering nor the soft shale between the shale clay and the hard shale can be had.

The table* of analyses on page 77 will show the composition of some Ohio ferruginous shales which might become available.

A typical ferruginous shale when examined by the rational method of analysis gave the following mineral analysis:

	Per cents.
Clay substance	62.27
Quartz	25.53
Feldspathic detritus	12.07

Owing to the high content of iron these shales, of course, produce dark colored cements, but many of them are very suitable for cement making purposes as far as the chemical composition is concerned.

Silicious Shales.—We have in Ohio no large areas of distinctly silicious shales, but many local deposits are available. Often where a transition from shale to sandstone is found the shale as it approaches the stone becomes more and more silicious. If this silicious dilution is fine-grained, the material becomes extremely valuable for cement making purposes; in fact we might say that it would be the ideal of a cement clay. In reality, however, the sand addition is frequently too coarse grained and the resulting shale is not any better than any clay mixed with sand. The locating of a suitable silicious shale is therefore a matter of local conditions; for instance, we might find a high bank of shale of which only a part is silicious, a strata only a few feet in thickness.

Rather extensive deposits of silicious shales are found between the horizons of the Bedford and Cuyahoga shales. The Berea grit, a sandstone, frequently carries 8 to 10 per cent. of alumina and possesses the shale structure, making it a valuable material for cement manufacture. Though the Berea grit does not always show this structure, it invariably accompanies the Bedford shale, being found above the latter. The grit is usually very fine grained and when burnt assumes a red color. Judicious mixing and grinding together of the Berea grit and Bedford shale would in many cases produce a most suitable basis for the making of Portland cement. This seems to the writer to be a point well worth looking into

*Prof. Edward Orton, Jr., Ohio Geological Survey, Vol. VII, Part I, p. 132.

Number.	Percentages of Constituents.									% Silica / % Alumina.	Molecular Ratio Silica : Alumina.
	Silica.	Alumina.	Ferric Oxide.	Lime.	Magnesia.	Potash.	Soda.	Combined Water.	Moisture.		
1	57.15	20.26	7.54	0.90	1.62	3.05	0.58	5.50	2.70	2.82	4.79 : 1
2	58.30	19.67	7.43	0.84	1.35	3.04	0.73	5.15	2.65	2.96	5.03 : 1
3	58.38	20.89	5.78	0.44	1.57	4.68	0.34	7.53	.....	2.79	4.74 : 1
4	57.28	21.13	8.52	5.79	2.13	.....	.....	5.22	.....	2.71	4.61 : 1
5	58.38	19.36	14.86	1.48	1.06	.....	.....	.....	.....	2.75	4.68 : 1
6	61.65	20.36	6.95	0.46	0.14	2.82	0.55	6.95	.....	3.03	5.15 : 1
7	52.19	14.61	10.00	.....	.....	.....	.....	5.62	12.62	3.56	6.05 : 1
Average	.....	.....	.....	.....	.....	.....	.....	.....	.....	2.95	5.01 : 1

No. 1. Shale mined at Glouster, Ohio, horizon of Cambridge limestone.
No. 2. Same shale with addition of one-fourth leached drift clay.
No. 3. Shale mined at Darlington, Muskingum county, Ohio.
No. 4. Bedford shale, Northern Ohio.
No. 5. Shale from Canton, Ohio, Putnam Hill horizon
No. 6. Shale of same horizon, near Canton, Ohio.
No. 7. Shale from North Industry, Ohio, Lower Mercer horizon.

at places where limestone is also found near by. The Bedford shale extends from Lake Erie down to the Ohio river. Starting from Cleveland, Independence (Cuyahoga county), the shale extends south through Crawford, Delaware, Franklin, Fairfield counties, and is found to crop out in large sections at Waverly and Piketon.

Sections of this material in Franklin county run about as follows:

Berea grit	0 to 30 feet.
Chocolate Bedford shale	10 to 40 feet.
Green olive Bedford shale	0 to 20 feet.

Calcareous Shales.—Where shales are in contact with limestone or highly calcareous materials we are apt to find them rather high in calcium carbonate, which might run so high as to convert the shale into a hydraulic cement material, as is the case at Defiance, where the natural cement stone has a distinct shale structure. Larger areas of calcareous shale in Ohio are not known to the writer.

Carboniferous Shales.—These differ from the other shales in the fact that they contain carbonaceous matter varying from one or two up to 12 or 14 per cent. The most prominent shale of this type is the Huron shale, of Devonian age, lying on top of the great limestone beds. In color the shale varies from a black to a dirty green. The black shale is very hard, tough and almost non-plastic and resembles roofing slate. Where it has been exposed to the weather it appears as a yellowish clay, full of thin flakes of harder material. These pieces are often rusty brown on the surface and still black in the core. The lower green layers of the shale are much softer and contain much less, frequently almost no carbon.

A piece of the black shale thrown into the fire burns for a few minutes. Its carbonaceous matter consists principally of bitumen, which volatilizes readily and burns like a rich gas. The amount of this material is from 2 to 6 per cent.

The iron in this shale owing to the large amount of carbon present is, of course, all in the lower state of oxization, being present as ferrous carbonate or ferrous sulphide.

This fact in connection with the large amount of organic matter makes this kind of shale exceedingly difficult to handle for the clay worker, though not interfering with cement making. While the bitumen is a great tribulation to the brick maker it would work beneficially to the cement manufacturer, inasmuch as the carbon would help burn the cement mixture, making a considerable saving in the fuel expense, provided, of course, that the chemical composition of the shale otherwise is satisfactory.

The following is an analysis* of the black Huron shale, sampled at Columbus:

*"*Ohio Geological Survey*," Vol. VII, Part I, p. 133.

	Per cents.
Silica	58.38
Alumina	20.89
Ferric oxide	5.78
Lime	0.44
Magnesia	1.57
Potash	4.78
Soda	0.34
Carbon	2.71
Chemical water, etc	4.82

In another sample of this shale there was found an iron content of 10.67 per cent. (as ferric oxide), of which 7.96 per cent. was ferrous iron, reported as ferrous oxide. The same shale was likewise found to contain 1.63 per cent. of sulphuric anhydride (SO_3) soluble in water.

From this the inference must be drawn that the material is liable to be too high in sulphur to be used as a satisfactory cement material. But that does not mean that this is true of all the shales; this point must be determined for every particular locality where this shale is found.

Plastic, Ferruginous Clays, Brick Clays, Weathered Shales.—As the shales succumb to the influence of the atmospheric agencies they gradually lose their shale structure and become again clays, with of course the same chemical composition, except that all oxidizable substances are converted into the higher oxygen compounds. Ferrous carbonate is decomposed and becomes ferric oxide, iron pyrites is changed to ferric sulphate. As a result we have in place of the hard mass showing a pronounced parallel structure a soft clay, possessing a much greater plasticity than did the shale. On the surface and outcrop of every shale deposit, we find, hence, plastic clay, and if the shale is suitable for cement-making by virtue of its chemical composition and fineness of grain the clay derived from it is much more valuable, since its softness renders it so easy and cheap to grind. In addition to this comes the uniformity of the composition, a property peculiar to shales, so that a shale clay is apt to be a material of magnificent working qualities.

Alluvial Clays.—As we have already seen, the clayey and sandy materials carried along by a stream are deposited according to their size and specific gravity dependent on the velocity. The swifter the stream flows the coarser will be the matter deposited by it. We call the comparatively fine rock matter deposited by a river alluvium.

Usually the rivers flow through a narrow plain within which the stream winds from side to side and over which the water spreads in times of flood. The larger the river the wider will be this plain. At the same time the river erodes for itself a deeper and deeper bed, so that extensive banks and terraces are formed on both sides of the stream.

The character of an alluvial clay is hence largely dependent upon whether the stream was flowing rapidly or slowly, whether it was a large or small, deep or shallow river, whether the course was straight or crooked. From this it follows that in looking for a suitable alluvial clay

for cement manufacture we ought to know something in regard to the old or present river drainage which produced it. If the old river bed indicates a narrow stream with a rapid fall it would be idle to expect to find in its valley a fine grained clay. In most cases the old river valley is outlined by the gravel beds or terraces (see figure 6), so that its

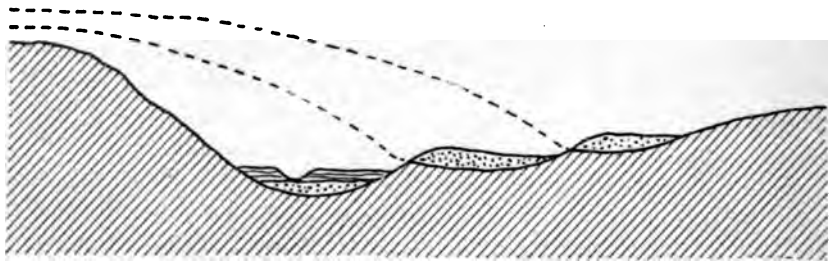

Fig. 6. River Terraces.

course can be followed with comparative certainty. If on the other hand the indications are that the stream was large and had a low velocity we have reason to expect that the fluctuation in the fineness of the clay material will be insignificant, and hence it is suitable as far as the physical characteristics are concerned. Again in a large river with somewhat greater velocity but with many curves and bends we should be encouraged to expect fine grained clay along the pools formed by the bends in which the water is in a state of comparative quietness and hence the particles deposited are very fine.

River deltas are a source of a great deal of the very finest material, since there the velocity of the current is smallest and the chance to deposit the load carried by the water is greatest.

It is important, therefore, that we should study and know the geological conditions under which the clays in question have been deposited. If found in an old river valley we should trace carefully all evidence in regard to the river now disappeared. If this were done much disappointment would be avoided. Frequently it has been found that a bed of very fine grained clay satisfactory in every respect degenerates at once into a coarse sandy clay or even gravel. It must be remembered that naturally the chemical composition will also vary with the introduction of coarse material. But if the problem of selecting suitable alluvial clays is attacked in this light it often is possible to find one corresponding to all the requirements.

According to the character of the rock detritus carried along we have alluvial clays of all possible mineral compositions, from almost all sand to practically all clay. In general, however, the alluvial clays used so extensively in brick making range in composition between 25 to 60 per cent. clay substance, 5 to 25 per cent. feldspathic detritus and 0 to 25 per cent. of quartz.

Chemically, the variations are just as wide, and hence it is easy to see that we can have alluvial clays high in lime, or iron, or silica, although as a rule the alumina is never high, due to the fact that the clay substance is usually low.

In the sandy varieties the total silica may be 90 per cent., in the calcareous the calcium carbonate may be 20 or 25 per cent. In the ferruginous clays the ferric oxide may be as high as 10 to 14 per cent.

The following analyses represent typical alluvial clays:

Ingredients.	Sample Number.		
	1	2	3
Silica	63.73	74.75	61.93
Alumina	17.17	12.55	19.87
Ferric oxide	5.85	5.28	7.83
Lime	0.58	1.28	1.61
Magnesia	0.97	0.85	0.77
Potash	2.33	2.27	2.38
Soda	0.67		
Chem. water	4.90	3.23	5.91
Moisture	2.96	.....	.....
$\frac{\% SiO_2}{\% Al_2O_3}$	3.71	5.96	3.12
Molecular ratio—Silica to Alumina	6.31 : 1	10.13 : 1	5.30 : 1

No. 1 is an alluvial clay from Columbia, Ohio.
Nos. 2 and 3 are clays quoted by Langenbeck as typical alluvial clays.

The rational analyses of Nos. 2 and 3 were found to be as follows:

	Per Cent.	
	No. 2.	No. 3.
Clay Substance	39.12	67.90
Quartz	52.54	21.57
Feldspathic Detritus	8.55	10.83

It is quite obvious that the composition of the clay substance in these clays cannot be as pure as that of refractory clays owing to the heterogeneous character of the mineral fragments from which the clays resulted. In clays Nos. 2 and 3 the clay substance had the following composition:

	Per Cent.	
	No. 2	No. 3
Silica	44.86	48.53
Alumina	30.50	28.48
Ferric Oxide	11.71	9.22
Lime	1 30	2.14
Magnesia	2.17	1.02
Potash Soda	1.20	1.92
Chemical Water	8 26	8.70
Ratio, Silica to Alumina	1.47	1.70
Molecular Ratio, Silica to Alumina	2.50	2.89

Glacial Clays.—The glacial or drift deposits cover at least two-thirds of Ohio in varying thickness.

"The line marking the most southern drift formation enters Ohio in Columbiana county, passes eastward through Stark into Wayne county, turning to the southward as far as Holmes county. From this point its general direction is southwesterly. It leaves the State in Brown county, crossing the Ohio river into Kentucky, a small part of which is included in the drift formation. A number of prominent points can be noted by which the boundary can be well designated. Newark, Lancaster and Chillicothe for examples are situated almost exactly upon the glacial boundary." (Dr. Edward Orton, Geol. Survey, Vol. VII, Part I, p. 38.)

Where does this material come from? We cannot now enter into a detailed exposition of the story of the drift clays and our explanation must be restricted to the statement that all glacial clays are a conglomerate mixture of native clays, shales, sandstone, limestone and various other rocks mostly of igneous origin, which have been brought from the north by the irresistible sheet of ice once covering so large an area of Ohio. We must keep in mind that the tremendous mass of ice not only ploughed up the old rocks, but also carried along those varied rocks which are peculiar

to northern Michigan and Canada. Besides this the ice, owing to its enormous weight, exerted great pressure on the surface and compacted it.

As is to be expected, the glacial or drift clays of Ohio are a heterogenous material of extreme irregularity of composition, containing bowlders of all sizes, sandy at one place and again full of limestone pebbles, besides many other extreme variations. We can reduce our treatment of the glacial clays to the statement that as such they are unfit for consideration as cement materials.

The only way by which they can be made workable by nature is redeposition, which may give rise to local deposits of great value for cement making. The bowlder clay must be washed by rivers or creeks into lakes where the fine mineral matter is deposited, giving rise to fine grained clays of more or less uniform composition. If the composition is suitable for the manufacture of Portland cement, having the proper silica-alumina ratio and being low in magnesia, such a clay is of great value and should be carefully explored. Its importance can, however, be only local, since it was deposited in a lake in a given locality under favorable conditions. All these clays have a tendency to be irregular in composition and must be watched carefully in winning them.

The table on page 84 gives analyses of several glacial clays:

Columbus drift clay analyzed by the rational method gave the following result:

	Per cents.
Clay subtance	33.60
Quartz	42.20
Feldspathic matter	20.18
Calcium carbonate	4.02

SANDSTONE AND SAND.

There may be cases in which the prevailing conditions demand the addition of silica as such to the Portland cement mixture and it may hence become necessary to look for a silicious material. It is evident that such a material must be fine grained and easy to grind if it is to become available for this purpose. The most suitable sandstone has already been mentioned as being an accessory of Bedford shale, namely Berea grit. Of course this stone is not everywhere suitable, it being in places very hard and difficult to grind, while again it may be coarse grained and irregular in composition. The fitness of a stone for cement purposes must be determined for each local deposit. The stone is frequently made more easily reducible by being heated in a vertical shaft furnace built exactly like a limekiln, and quenched while hot by a stream of cold water. It would not be necessary to raise the temperature very high, a good red heat being ample to accomplish the desired result.

Though sandstone may not be available, sand is found in so many localities that a satisfactory kind will be accessible almost every where It is evident that the sands also differ greatly in physical and chemical

Number	Percentages of Constituents.								% Silica. / % Alumina.	Molecular Ratio $SiO_2 : Al_2O_3$
	Silica.	Alumina.	Ferric Oxide.	Lime.	Magnesia.	Potash.	Soda.	Combined Water		
1	69.77	18.33		3.25	0.64	2.74	0.48	4.90	3.81	6.48 : 1
2	50.70	17.00		9.41 (as carbonates)	4.66	.....	.....	.....	2.98	5.07 : 1
3	64.85	17.98	5.92	2.24	1.40	.....	.....	4.98	3.60	6.12 : 1
4	65.41	16.54	6.06	2.22	.....	0.43		7.46 (Loss)	3.95	6.72 : 1

Clay No. 1 is glacial clay dug on the campus of Ohio State University.

No. 2 is clay used in manufacturing Portland cement at Harper, Ohio.

No. 3 is a redeposited lacustral clay used largely in making cement, found at Millbury, Ohio; much of it is shipped to Michigan. Analysis from Geological Survey of Michigan, Vol. VIII, Part III, p. 229.

No. 4 is leached glacial clay, found at Sandusky, Ohio, and used in making Portland cement. Quoted in Tonindustrie Ztg., Vol. 24, No. 151.

respects and must be examined as to their composition and extent of the deposit. The ideal source of sand would be the material known as molding sand, which is very fine grained, though carrying considerable iron and alumina.

LIME.

A rough classification of lime materials might be made as follows:

1. Crystalline calcium carbonate, crystalline character well developed.
2. Dense, glistening.
3. Dense, dull, non-crystalline, often impure.
4. Amorphous, porous, earthy, often impure.

The gradations from the chemically pure calcium carbonate which was formed under favorable natural conditions to the most impure calcareous materials, like the calcareous clays, are not abrupt. Sedimentation of clayey materials was always coincident with the precipitation of the lime to a greater or less degree, and hence we can look for pure carbonate only in exceptional cases. A good deal of the pure lime is obtained by resolution and precipitation, or by taking up of lime by animal life, resulting in the building up of banks of animal remains (coral banks).

Crystalline Calcium Carbonate.—Calcium carbonate in its state of greatest purity is represented by calcite, whose specific gravity is 2.72 to 2.90. Another form of crystalline calcium carbonate, the aragonite, crystallizing in the rhombic system, has a specific gravity of 2.9 to 3. While on burning calcite calcium oxide is obtained which slakes in water with the evolution of heat, aragonite when burnt increases apparently in volume and breaks up into an asbestos-like matted mass of needle-like crystals. When powdered and moistened with water the substance does not heat, but breaks down slowly to a powder. It is harder than calcite, but more soluble in water.

The principal forms of crystalline calcium carbonate are the coral rocks, the white or grayish coarse-grained limestones, showing the glittering calcite grains very distinctly, the calcareous masses deposited from solution in limestone caves (stalagmites, stalactites), travertine, etc. When metamorphosed by the action of heat and pressure, limestones may be changed by recrystallization to marbles, which are characterized by an extremely uniform grain, giving them a granular structure.

The Dense, Glistening Forms.—The dense, glistening limestone rocks are as crystalline as the preceding materials, but the crystallization is not as well defined and the individual crystals are, as a rule, too small to be identified. These rocks form the most important source of lime for the lime industry, and hence are of much greater economic value than the crystalline rocks of the first section. These limestone occur in massive beds and are extremely dense, producing the greatest amount of caustic

lime per unit volume, but requiring also more heat in the burning. The rocks are liable to be contaminated with varying smaller amounts of impurities and especially may be associated with the carbonate of another alkaline earth, magnesia. But as a rule the clayey impurities are small in amount. On breaking the rocks show a splintery or conchoidal fracture. The specific gravity varies from 2.6 to 2.8. When treated with cold hydrochloric acid it dissolves readily, except in the presence of a larger amount of magnesium carbonate; the clayey matter is practically all left behind. No fixed limits can be drawn for the composition of these rocks; it is bound to vary, depending on the conditions which prevailed during the formation period. If precipitated in muddy water, the limestone is certain to contain clay; if thrown down in concentrated aqueous solutions, as in inland lakes or bays of the sea, other salts like the magnesium compounds are bound to crystallize out with the lime.

Dense, Dull, Non-Crystalline Limestone.—These are principally lime deposits produced in muddy water, and hence are high in clay. It is quite evident that the variety of composition of these materials must be wide, since the impurities and the clayey substances may represent almost any possible combination of materials. As the clayey constituents increase the limestone changes to cement rock and finally merges into a calcareous shale. The rocks of this division are, as a rule, very hard and dense and possess a dark blue or dark gray color. Frequently they show shale structure, caused by mountain pressure. The calcium carbonate is very often associated with magnesium carbonate, so that the rock is really a clayey dolomite. Carbonaceous matter is frequently deposited in these rocks, from graphitic carbon to bitumen and volatile hydrocarbons. Some of the so-called "stink stones" owe their fetid odor to petroleum compounds or to hydrogen sulphide. Limestones of this character are often high in iron sulphide (pyrites), which accelerates the decomposition of the rock by weathering, spoiling it for building purposes.

To the dull, hard limestone divisions belong also the rocks having a concretionary or oolitic structure.

Many sedimentary rocks show a concretionary structure. This may be part of the original sedimentation or may be due to subsequent segregation around a center.* This structure is produced by the collection of mineral matter, say calcium carbonate, from the surrounding rock or from without around some center so as to form a nodule, large or small, as the case may be. If these nodules are close together they may form a practical source of lime, but this is usually not the case. Oolite consists of more or less round grains of calcium carbonate, each grain having been deposited in concentric shells around some center. The oolitic rocks have the appearance of a mass of fish eggs, as, for instance, the well-known Indiana oolitic stone.

*Geikie, *Text Book of Geology*, page 510.

Amorphous Calcium Carbonate.—This forms a large class of materials of great practical importance. Its variety of composition is very great. The most representative materials of this class are chalk and marl. The former is a fine light-colored material derived from the remains of foraminifera, echinoderms and other marine organisms. Owing to its extreme fineness it becomes readily available for chemical reaction. Thoughout the chalk-beds flint-stones are found which either have a direct organic origin or have been formed by the precipitation of silica.

The term marl is applied to calcareous materials formed in connection with fresh water lakes or basins by the precipitation of lime, obtained by the leaching out of limestone rocks. Various theories are advanced in regard to the formation of marls, but none of them have been proven beyond doubt, yet the chemical theory seems to come closest to the truth. The extreme fineness of grain of marls renders them especially suitable for cement-making purposes, and hence large manufacturing districts have been built up around the great marl areas of the country. In addition to the fineness of grain of marls, the fact that their calcium carbonate is amorphous is a material factor in bringing about ready chemical combination. The one great drawback is the extreme irregularity of composition, which causes them to show great fluctuations within narrow areas, and hence calls for caution and thorough exploration of newly developed marl deposits.

THE LIME RESOURCES OF OHIO AVAILABLE FOR PORTLAND CEMENT MANUFACTURE.

PRELIMINARY STATEMENT BY PROF. EDWARD ORTON, JR., E. M. AND S. V. PEPPEL, B. SC.

The resources of Ohio in raw material for the manufacture of Portland cement are great. Fuel, limestone and clay are here in abundance, together with some of the marls which form so important an element in the lime supply of Indiana and Michigan.

The ability of Ohio to furnish limestone of a desirable composition and in quantities sufficient to justify economic development for the manufacture of Portland cement is much greater than is the general belief. Almost all of the Lower Silurian formation above drainage in Ohio is available. Many points on the Clinton horizon furnish beds from 7 to 15 feet thick which are of desirable composition. A few places on the northern portion of the Corniferous limestone may be used for a thickness of from 3 to 7 feet. Several horizons in the coal measures have stone of the proper composition, namely, the Maxville, the Ferriferous and the limestones over the Pittsburg coal horizon, and a small area, 30 to 50 feet, under the Pittsburg coal in Athens county. Twenty-three counties, at some point in each, furnish a limestone which can be made into a good Portland cement, and nearly all of these have quantity sufficient to be worked with economy.

Limestone, or mixtures of limestone and shale within the following limits of composition, will be found to be very close to the composition desired in a Portland cement mixture:

	Per Cents.
Silica	15–16
Alumina and ferric oxide	6– 7
Calcium carbonate	74–76
Magnesium carbonate	0– 4.5

The ingredient which we must watch with greatest care is the magnesium carbonate. It must not go much beyond 4.5 per cent., and the lower it is the better. If the silica and alumina are too high, we can correct this by throwing out a little clay or shale or adding a little high-calcium limestone.

Bearing the above statement in mind, a scrutiny of the tables of analyses given later will show that there are many places where limestone of great thickness, mixed with shale in thin strata, the average of which comes very close to the limits named above, may be obtained.

The samples, the analyses of which are given later, were in most cases so taken as to represent a cross section of the strata. A section was

cut so as to approximate as nearly as possible what would be obtained by taking out a core with the diamond drill. The resources of each horizon are given herewith:

LIMESTONES.

Lower Silurian. —The Lower Silurian or Hudson river group consists of layers of shale and limestone interstratified. The shale varies from less than 1 inch in thickness to 4 feet and the limestone from a few inches to 14 feet. It is seldom that two layers are found, one or the other, without a shale parting. The shales are always silicious, with the silica or quartz rather fine grained, which is a desirable feature for Portland cement manufacture. This group of limestones frequently offers faces of 50 to 100 feet with comparatively little stripping. This is the largest single body of limestone in the State, which will make Portland cement. There will be but few localities in this formation, which will not furnish stone of a desirable composition, as the table of analyses will show.

This formation can be found in a few ridges in Miami county, in Preble, Montgomery, Clark, Green, Butler, Warren, Clinton, Hamilton, Clermont, Highland, Brown and Adams counties. The limestone is a dark, blue gray to purple, highly crystalline stone. The shales are blue, gray, and brown. (See table I at the end of the chapter.)

Clinton.—The Clinton horizon is the only other horizon of the older rock formations of the State of much commercial importance for the cement industry. The Clinton is found almost everywhere along the border of the Hudson river groups, and is nearly always overlapped by the next formation above, which is the Niagara. The Clinton is a highly crystalline rock of varied colors, and compositions, and of variable thickness. Sometimes there is a little shale interstratified, but as a rule not. The upper layers are always characterized by the abundance of crinoid fossils. While it is the most irregular of the lower limestone formations, it is readily recognized, and notwithstanding its varied composition quite a number of locations furnish stone of excellent quality for cement manufacture, as is shown in the table of analyses. It frequently happens that the lower beds of this formation are highly magnesian, and it is not uncommon for it to be highly magnesian throughout. At Lumberton, Clinton county, there is 12 feet of stone, with less than 2 per cent. $MgCO_3$, lying on top of 5 feet with 29.94 per cent $MgCO_3$. At Lynchburg, there is 14 feet 6 inches with a little over 1 per cent. of magnesium carbonate on top of 5 feet with 12 per cent. of $MgCO_3$ and at Leesburg, Highland county, not many miles from the former location, it varies from 25 to 41 of the $MgCO_3$.

The great majority of this stone which is of proper quality is from 7 to 15 feet thick, and so located that if more than 10 to 20 acres were to

plied from an opening in the Putnam Hill limestone, which is there 8 feet in thickness. The following is the composition of the stone:

	Per Cent.
Silica	4.12
Alumina	1.86
Ferric oxide	1.20
Carbonate of calcium	91.16
Carbonate of magnesium	1.63
	99.97

Localities where this stone is of suitable composition are not rare, but no other locality can be cited where the stone assumes a thickness at all sufficient for any extensive cement industry. It is usually of dense gray limestone, of 2 to 4 feet in thickness, which could not be profitably mined or stripped.

Ferriferous.—The Ferriferous limestone, especially in its southern exposure, is a very important and promising source of cement stone. The area covered by this stone, in its exposures above drainage, comprises an area about 6 to 8 miles wide and 40 or 45 miles in length, and amounting to about 300 square miles. In the western edge of this area, it is too thin to mine well, and its position near the tops of the hills makes the areas small. But on the eastern edge the areas are large, and but little dissected by valleys, and the stone is covered by strata suitable to make a good roof for mining it. Its thickness runs from 4 feet in the thin exposures to 10 feet in the best; 6 to 8 feet are its usual development. It can be won by mining or by stripping and benching around the edges of the hills. The point where the latter method ceases to be profitable marks the point where mining becomes possible. The chemical character of the stone is exceptionally well suited to cement manufacture. It is low in magnesium everywhere; it is usually well over 90 per cent. of $CaCO_3$ and frequently contains over 95 per cent. of this ingredient. Its iron is generally low, favoring a light colored cement. (See table V at end of chapter.)

This stone is now being used as the basis of cement manufacture at some three well equipped works, which are turning out an excellent product.

This stone on the northern edge of its field becomes thin and irregular and finally disappears north of Creola, Vinton county, and shortly afterwards the Putnam Hill limestone makes it appearance, in passing to the northeast.

Lower Kittanning.—There is no other constant or well marked horizon of limestone of which sufficient quantity is found to be commercially interesting for several hundred feet above the Ferriferous horizon. Several formations swell up locally and offer for a limited area a

possible source of cement supply. Of such a character is the stone at Lisbon, Columbiana county, where it has been used as the basis of a "natural cement" industry for years past. It is only 34 inches thick, occurring on the horizon of the lower Kittanning coal. It analyzes as follows:

	Per Cent.
Silica	17.76
Alumina	7.94
Ferric oxide	1.86
Calcium carbonate	66.25
Magnesium carbonate	2.82
	96.63

Middle Kittanning.—A similar stone at Rodgers, in the same county, having a thickness of 4 feet 6 inches, has the following composition. It is obtained just under the middle Kittanning.

	Per Cent.
Silica	25.44
Alumina	10.62
Ferric oxide	2.34
Calcium carbonate	55.59
Magnesium carbonate	2.14
	96.13

Both of these stones are won by mining.

Freeport.—The Freeport limestone occurring on the horizon of the coal veins of that name are generally very impure, either being cherty, or clay like. No instance is known to the writers where this stone seems promising.

Cambridge.—The Cambridge limestone, located approximately 100 feet above the Freeport horizon, through a well marked horizon so far as regularity and persistence is concerned, is generally thin and worthless for the present purpose. Like most of the coal measure limestones, its origin favored its occasional growth into relatively thick pockets and masses, but usually it is a thin layer, even degenerating into a stratum of bowlders separated by clay. At Cambridge, in Guernsey county, it is reported as of 8 feet thickness and as having been worked for lime. It is certainly not a wide or important formation for this use.

At the head of Cannon's Creek in Lawrence county, the Cambridge stone thickens up into a ledge of some 6 feet or so, quite cherty in character. A careful cross-section of this exposure analyzed as follows:

	Per Cent.
Silica	38.00
Alumina	6.78
Ferric oxide	1.90
Calcium carbonate	50.60
Magnesium carbonate	1.73
	99.01

humus. But in Indiana and Michigan, large lakes are still in existence, though much shrunken in area, whose banks and bottom are covered with the marl. In some cases, extensive operations are undertaken to drain these lakes to get at the marl and in other cases the use of dredges is resorted to bring it up from the bottom.

The origin of the marl has been discussed a great deal. It is now ascribed to the action of fresh water algæ, which precipitate it or throw it down from solution. Whether this be the truth or not, its close and intimate connection with fresh water lakes is too patent to be denied. In searching for it, therefore, the obvious method is to observe the locality for flat meadows or marshes, which have the appearance of having been at one time the site of glacial lakes. The water sheds between the rivers flowing north to the lakes and south to the Ohio forms a promising territory for such explorations, but many of these marl covered lake-sites exist all through the drift covered area of the State, more abundantly in the northwestern third.

The composition of the marl is eminently well suited to cement. It consists of the amorphous or organic form of calcium carbonate, mixed with varying amounts of soil, sand, humus, snail shells, etc. Frequently the percentage of calcium carbonate reaches 96 to 98 per cent., while magnesia, the bane of Portland cement, is practically absent. It is a soft, damp, gray earth somewhat like bulk sugar in appearance; it has little plasticity when worked up with water like a clay, and still less hardness or strength when dried. It dissolves in any acid, even vinegar, with much effervescence or foaming. Many farmers, owning land on which it occurs, do not know what it is, or of its possible uses; others do not care to sell their land for cement purposes, as these old swamp beds are usually rich and productive for farming.

Ohio's known areas of marl are very limited compared to those of Michigan and Indiana. It is not probable that any future discoveries will bring our deposits up to theirs in size or importance. But it is wholly probable that our resources can be greatly extended by systematic and intelligent search. Nothing of the sort has been yet undertaken. A two inch boring auger, with extensible handle, is about all the equipment that is needed, as these deposits are always superficial and under but slight cover of clay or soil. By driving over the country, studying its topography, searching out its old depressions, and drained marshes, it would be possible without doubt to bring many deposits to light.

The marl beds of northwestern Logan county, lying between Harper and Rushsylvania, are typical deposits. These deposits support two Portland cement industries, the Buckeye and Alta plants. An analysis of the marls shows:

	Per Cent.
Silica	8.75
Alumina, Ferric oxide	2.78
Carbonate of calcium	79.21
Carbonate of magnesium	2.67
	93.41

This analysis is characteristic, though the amount of clay mixed with the marl causes its proportion of silica and alumina to rise a little at the expense of the carbonate of lime from time to time. As clay must be added in any case, this is no disadvantage except possibly in keeping uniform mixtures. The known extent of this field is not great and is under control of the two companies now established.

Another marl area is in northeastern Sandusky county and northwestern Erie county. The Sandusky Portland Cement Co., located at Bay Bridge, has nearly exhausted its bed of marl which was not of large proportions originally. It has supplied material for a considerable industry for more than a decade. The Castalia Portland Cement Co., at Castalia, three or four miles south of Bay Bridge, has a much larger bed and a larger plant.

Travertine.—Associated with the marl beds in the Castalia district is a layer of Travertine, or calcareous tufa, deposited probably from former overflows of the great Castalia spring, which wells forth in volume sufficient to make a small stream. This underground river, for it is nothing else, maintains at present a considerable lake or pond, and in times past probably made a much larger area of swamp land. Over this area, the travertine has been deposited, in some places as much as three or four feet thick, though generally much less. It is substantially pure carbonate of lime, showing a content of 99.4 per cent calcium carbonate.

It is deposited as carbonate, from the breaking down of calcium bicarbonate as it emerges from the underground water-course, and is exposed to the air, heat and motion of the stream. Though travertine can hardly be called a regular source of Portland cement material, it is used at the Castalia works with very excellent results.

TABLE I.—Analyses of the Limestones.

Record number of sample	Locality of Quarry.	Thickness and relative position of stratum represented by this sample.
83	Adams Co., Manchester	From top layer down 21 feet
84	" " "	Next 12 feet below sample 83
85	" " "	From water level, up 20 feet
86	Brown Co., Georgetown	From top layer, down 16 feet, 6 inches
87	" " "	Next 23 feet below sample 86
88	" " "	Next 50 feet below sample 87
89	" " "	Next 26 feet below sample 88
90	" " "	Next 30 feet below sample 89
66	Butler Co., Excello	From top layer, down 10 feet 6 inches
65	" " "	Next 10 feet 6 inches below sample 66
58	" " Hamilton	From top layer, down 11 feet
59	" " "	Next 15 feet below sample No. 58
57	" " "	Next 15 feet below sample 59
56	" " "	Next 8 feet 6 inches below sample 57
55	" " "	Next 1 feet below sample 56
91	Clermont Co., Bethel	From top layer, down 18 feet
78	" " New Richmond	From top layer, down 20 feet
79	" " "	Next 15 feet below sample No. 78
76	Hamilton Co., Cincinnati	From top layer, down 8 feet
72	" " "	Next 18 feet below sample 76
73	" " "	Next 17 feet below sample 72
74	" " "	Next sample below sample 73
75	" " "	Next 13 feet below sample 74
77	" " "	From 85 to 107 feet from top of quarry
92	" " "	Next 22 feet below sample 77
93	" " "	Next 19 feet below sample 92
71	" " Glendale	From top layer, down 25 feet
70	" " "	Next 40 feet below sample 71
69	" " "	Omitting 3 feet, next 20 ft. below sample 70.
68	" " "	Next 11 feet below sample 69
67	" " "	Next 13 feet below sample 68
54	Preble Co., Camden	From top layer, down 10 feet
53	" " "	Next 20 feet below sample 54
52	" " "	Next 20 feet below sample 53
51	" " "	Next 12 feet 6 inches below sample 52
50	" " "	Next 12 feet 6 inches below sample 51
103	Warren Co., S. Lebanon	From top layer, down 50 feet
102	" " "	Next 40 feet below sample 103

TABLE II—Analyses of the Limestones

94	Adams Co., Newport	From top layer, down 21 feet
95	" " "	Next 10 feet below sample 94
L-2	Clark Co., New Carlisle	Average of quarry
110	Clinton Co., Lumberton	From top layer, down 12 feet
115-116	" " Lynchburg	From 8 feet 6 inches to 14 ft. 6 in. below top.
131	Greene Co., New Jasper	From 5 feet to 12 feet below top
L-1	" " Osborn	Best Rock
L-2	" " "	Rejected Rock
L-	Miami Co., Piqua	Surface
47	Montgomery Co., Centerville	From top layer, down 9 feet
60-63	Preble Co., Eaton	From 2 ft. 4 in. to 14 ft. 10 in. below top
35	" " New Paris	From top layer, down 2 feet

of the Lower Silurian or Hudson River Formation.

Constituents.					Total.	Remarks.	Serial Number of Sample.
Silica.	Alumina.	Ferric Oxide.	Carbonate of Calcium.	Carbonate of Magnesium.			
9.30	3.04	1.30	82.50	1.93	98.07	A gap between samples 84 and 85 was not sampled.	83
10.10	3.14	1.30	83 50	1.51	99.55		84
7.86	2.95	0.75	85.60	2.48	99.64		85
13.20	4.46	1.30	78.05	2.36	99.37	Total section sampled was 145 feet 6 inches.	86
32.80	9.12	2.30	49.69	4.12	97.99		87
32 34	8.69	2.45	50.00	4.15	97.63		88
31.60	10.97	2.85	47.25	5.00	97.67		89
45.36	15.24	3.90	26.25	5.06	95.81		90
28.94	10.00	2.90	52.95	2.65	97.49	10 feet from bottom of 65 to drainage.	66
31.80	10.95	3.25	48.40	3 25	97.65		65
36.00	12.36	3.70	41.60	3.57	97.23		58
29.96	9.55	3.05	49.80	3.06	95.42		59
33.86	11.56	3.50	44.00	3.72	96.64		57
26.10	8.44	2.30	56.80	3.58	97.22		56
34.80	11.62	2.80	42.50	4.72	96.44		55
18.74	6.80	1.90	68.50	3.06	99.00	Near top of H. R. Formation.	91
38.80	14.64	4.10	35.00	3.07	95.61		78
22.70	9.00	2.00	60.40	3.13	97.27		79
33.50	12.00	3.70	43.35	2.65	95.20	A gap of 12 feet was not sampled between Nos. 75 and 77.	76
20.66	7.74	2.10	63.70	3.58	97.78		72
30.28	10.30	2.40	49.60	4.46	97 04		73
33.08	10.78	2.80	46.60	4.19	97.45		74
30.00	9.80	2.30	51.45	3.75	99 30	Section represented in full is 148 feet thick.	75
36.84	11.14	3.30	40.90	4.15	96.33		77
38.00	13.80	2.80	38.72	3.80	96.62		92
25.04	9.38	2.80	58.08	3.02	98.32		93
24.26	7.99	2.65	60.40	2.80	98.10	A gap of 3 feet 65-68 feet below top of quarry was not sampled.	71
29 80	10.05	2.55	50.95	4.40	97.75		70
38.30	13.35	3.65	35.90	4.84	96.04		69
31.30	11.47	3.25	45.00	6.10	97.12		68
52.38	18.64	4.60	13.20	5.36	94.18		67
9.70	4.31	0.85	80.40	3.09	98.35	Total rock face-sampled, 75 feet.	54
15.28	6.05	1.25	70.35	5.34	98.27		53
13.16	5.15	0.75	75.90	3.30	98.26		52
14.60	5.25	1.55	72.30	4.37	98.07		51
11.62	4.84	0.80	76.70	4.54	98.50		50
23.30	9.11	2.05	60.08	3.28	97.82	Total rock face sampled, 90 feet.	103
29.00	9.57	3.15	52.63	3.52	97.87		102

of the Clinton Formation.

14.80	5.62	2.34	71.40	3.87	98.03		94
16.84	1.78	1.36	76.80	2.64	99.42		95
0.70	0.41	.....	97.14	1.21	99.46		L-2
1.80	0.85	0.75	93.90	2.78	100.08		110
11.03	0.92	0.82	85.96	1.11	99.85	Average.	115-116
9.30	4.38	0.60	81.92	3.24	99.44		131
1.64	0.36	.....	97.09	0.82	99.81		L-1
0.83	0.29	.....	96.80	2.07	99.99		L-2
0.45	0.26	.....	95.03	4.35	100.09		L-
4.02	2.28	0.52	88.95	3.59	99.36		47
0.81	0.82	0.24	94.21	3.79	99.89	Average.	60-63
1.52	1.00	0.60	95.10	1.80	100.02		35

TABLE III.—Analyses of the Limestones

Serial number of sample.	Locality of Quarry.	Thickness and relative position of stratum represented by this sample.
3	Franklin Co., Columbus.....	From 14 ft. 8 inches to 53 ft. below top.
—	" " "	Siftings from crusher, run of quarry.
L-1	Kelly's Island.....	Extra Cap Rock.
22	Lucas Co., White House.....	From top layer, down 7 feet.

TABLE IV.—Analyses of the Limestones

1	Perry Co., Fultonham.....	Top 12 or 15 feet, to water level.
61	" " White Cottage...	Top 9 feet, 3 feet to water level.
54	" " Maxville.....	White or gray stratum, 4 feet thick.
53	" " "	Top or Building Rock, 2 feet thick.

TABLE V.—Analyses of the Limestones

—	Jackson Co., Cornelia Fce. ..	Average of 16 Analyses.....
14	" " Kitchen Sta. ..	Cross section of stratum, 7 feet.....
35	Lawrence Co., Bartles St....	Cross section of vein, 7 feet 6 inches.....
—	" " Cal. Hollow...	From Campbell's quarry.....
—	" " Eliz. tp.....	Burke's Mine. Furnace Co.'s Analysis.....
—	" " "	Holly's Mine. Furnace Co.'s Analysis.....
—	" " "	Riley's Mine. Furnace Co.'s Analysis.....
—	" " Hang. Rock ..	Books of H. R. Iron Co.'s Furnace.....
—	" " " " ..	Burgess tract, average of ten analyses.....
—	" " " " ..	Bradshaw Entry.....
—	" " " " ..	School House Entry.....
—	" " Hog Run.....	Section 25. Furnace Co.'s Analysis.....
33	" " Olive Fce.....	Cross section of vein, 6 feet 9 inches thick....
—	" " Peter Cave ...	Mines of E. B. Willard.....
—	" " Pine G. F'ce..	Hanging Rock Iron Co.....
37	" " Steece P. O....	Cross section of vein, 6 feet 6 inches thick....
38	" " " "	Screenings from crusher.....
180	Mahoning Co., Lowellsville..	From top layer, down 14 feet.....
179	" " "	Next 5 feet below sample 180.....
19	Scioto Co., Eifort Sta.....	Cross section of vein as mined, 5 feet thick....
20	" " "	Drillings from Power Drill Holes.....
—	" " "	Average of 9 Analyses, Alma Cement Works..

TABLE VI.—Analyses of the Limestones

141	Athens Co., near Amesville..	14 feet 6 inches thick above Crinoidal.....
36	" " " "	13 feet thick, above Pittsburgh Coal.....
143	" " Canaansville.....	14 feet 6 inches thick, above Pittsburgh Coal.
172	Belmont Co., Henrysburg....	7 feet thick, above Pittsburgh Coal.....
153	Guernsey Co., Cumberland ..	7 feet thick, under Meigs Creek Coal.....
176	Jefferson Co., Steubenville...	12 feet thick, above Crinoidal limestone.....
139	Washington Co., Wesley Tp.	15 ft. 6 in. thick, above Pittsburgh Coal.....
140	" " " "	11 feet thick, above Pittsburgh Coal.....

of the Carniferous Group.

Constituents.					Total.	Remarks.	Serial Number of Sample.
Silica.	Alumina.	Ferric Oxide.	Carbonate of Calcium.	Carbonate of Magnesium.			
2.30	0.70	trace	91.66	6.06	100.72		3
2.63	0.83	.....	89.23	6.56	99.25		—
0.85	0.27	.....	97.28	2.00	100.40		L-1
1.24	0.69	0.05	95.25	3.47	100.70		22

of the Subcarboniferous Formation.

2.80	1.16	.....	92.80	2.13	98.89		1
3.04	1.54	0.40	92.92	1.21	99.11		61
6.14	1.40	0.40	90.96	0.90	99.80		54
16.34	1.70	1.00	80.35	0.68	100.07		53

of the Lower Carboniferous Formation.

.....	....	.....	80.90	....	.....		—
13.62	2.45	.....	82.30	0.82	99.19		14
0.74	0.24	1.30	97 35	0.33	99.96		35
0.98	2.15	.....	94.65	1.84	.....		—
0.41	0.86	0.78	93.28	4.66	.....	SO_3 0.78	—
1.30	0.86	.....	By diff	3.81	.....	SO_3 0.44	—
0.52	0.80	.....	94 19	4.49	.....		—
0.76	....	.....	96.87	....	.....	P=trace.	
3.30	6.20	with Al_2O_3	88.50	0.75	.....		—
0.76	1.50	with Al_2O_3	96.83	0.84	.....		—
1.10	3.20	5.25	88.70	1.60	.....		—
1.96	....	1.98	91.32	0.91	.....		—
1.52	1.86	0.70	95.40	0.53	100.01		33
0.23	0.50	1.30	96.83	1.00	.....		—
1.00	1.00	2.00	94.30	1.53	.....		—
3.26	0.90	1.30	94.16	0.85	100.47		37
22.26	1.05	1.55	75.07	0.20	100.13		38
2.58	0.68	0.70	93.50	1.64	99.10		180
2.20	0.54	0. 4	94.69	0.71	98.84		179
1.76	2.03	.....	94.50	0.80	99.09		19
0.53	1.55	.....	95.62	0.81	98.41		20
.....	....	.....	93.50	....	.....		—

of the Upper Carboniferous Formation.

4.62	1.44	1.00	90.90	1.60	99.56		141
22.90	8.17	2.07	62.29	2.69	98.12		136
14.50	4.56	1.40	76.78	1.21	98.45		143
3.14	0.74	0.90	92.48	1.84	99.10		172
7.24	1.48	1.20	87.47	2.40	99.79		153
12.50	10.11	4.19	61.10	5.86	93.76		176
25.28	8.47	1.87	58.17	3.70	97.49		139
14.32	4.82	1.66	73.67	5.20	99.67		140

CHAPTER III.

THE CHEMICAL AND PHYSICAL EXAMINATION OF CEMENT MATERIALS.

This subject will be taken up in the order of the classification adopted in the beginning. In treating the various methods of examining the materials we must bear in mind that we are to distinguish between scientifically exact and technical methods. Though the first are of great value in their place, they cannot be followed very closely in practice where rapidity is one of the great considerations. We must therefore keep this fact well before us. Another fact to be realized is the close connection between certain chemical and physical methods which go hand in hand and bring to light important relations which are not brought out by chemical or physical methods alone.

Prospecting and Sampling.—In investigating a new property for cement raw materials, it must be realized that the best methods of examination are of no value whatever unless the samples analyzed represent truly the character of the deposit. The guiding principle should invariably be that the less homogeneous a deposit is, the more samples must be taken and the more carefully must the work be done. The writer could cite a considerable number of examples where neglect to make a proper preliminary examination has resulted in the ultimate loss of thousands of dollars. Investors who are willing to put enormous capital into new plants often seem unwilling to spend a few hundred dollars for a preliminary mineral survey of the property. It is difficult to sympathize with such people thus rushing into financial disaster.

There seems a feeling, almost general among a certain class of small capitalists and business men, that the advice of a technically trained expert is either unsafe or unnecessary or both. Large financiers have gotten well beyond this stage and seldom move in any mineral enterprise until all has been done that the best and most skilful mining engineers can do, in disclosing the facts and prospects. But the business man who has made a little money in his own line, in which his judgment is skilled, seems imbued with an equal confidence in his judgment in some other field of which he knows nothing. The mineral industry, which above all others requires close and accurate technical supervision to attain, is the most favored field of these inexperienced and self-confident investors, and the loss annually suffered in this way from ignorant and ill-advised investment is simply beyond belief.

Strangely enough, the opinions of men who are obviously crude and ignorant, and whose opinions would carry no weight in any other connection, are often taken in establishing mineral industries, on the basis of their *practical experience,* while that of trained experts is condemned as *theoretical.* Even the word of interested persons, not possessing a rudimentary knowledge of technical matters, is readily believed by otherwise well-balanced conservative business men. The American habit of "booming" towns and localities has had a great deal to do with this reckless kind of work.

In looking for a suitable clay material the experienced prospector makes use of all natural and artificial excavations, such as gullies, river banks, railroad cuts and quarries, for determining the character of the rocks in a certain locality. He watches every clay outcrop, and by applying the rudiments of geological knowledge is usually able to trace down the available clay beds. With the help of the geological reports and maps, and especially with the assistance of the excellent topographical survey maps of the U. S. Geological Survey, the method of the attack is easily outlined.

If a random sample of a clay outcrop has shown a satisfactory composition and is promising in regard to its physical characteristics, an opening should be made into it, removing the surface clay, and a sample taken from the material within the bank. If this should likewise prove satisfactory, the bed is attacked at several places, examined, and finally a survey is made of a tract which affords enough material for the capacity of the factory which it is intended to erect. The area of the land is plotted and a topographical survey made. Now the map is divided into squares whose sides should range between 50 and 100 feet in length, depending on the different thicknesses of the deposit. If the latter is thick, say 30 or 40 or more feet, the square should be taken with sides of about 50 feet in length; if it is but several feet deep, they should be 100 feet, since the area to be examined in this case is so much larger. At the center of every square a test hole is sunk and the material brought up by the drill put aside for analysis. If at the depth drilled the clay is apparently of the same structure, color and general appearance, a sample need only be collected for every ten feet of depth; if, however, on drilling, various materials are found, a sample must be set aside for each different material.

By means of these drill holes sections can be plotted cutting the center of the area at right angles, one section passing through the deposit, say from east to west, and the other from north to south. After having plotted these sections to scale on a map the total amount of the different kinds of clay available, in cubic feet or cubic yards, can then be calculated with sufficient accuracy.

It is hardly necessary to state that the samples must be kept in suitable, tight receptacles, carefully labeled.

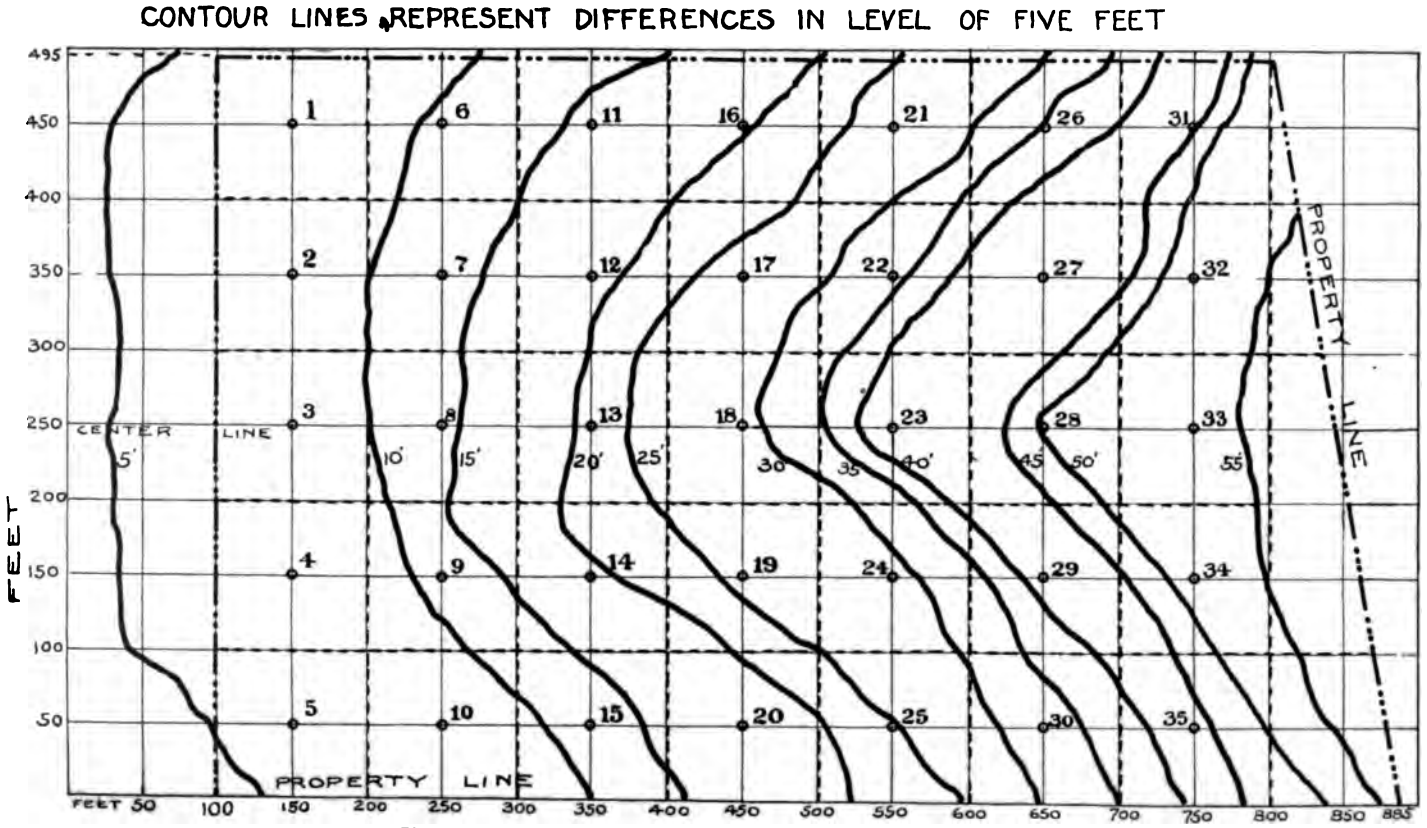

Fig. 7. Map of a property for the purpose of prospecting for clay.

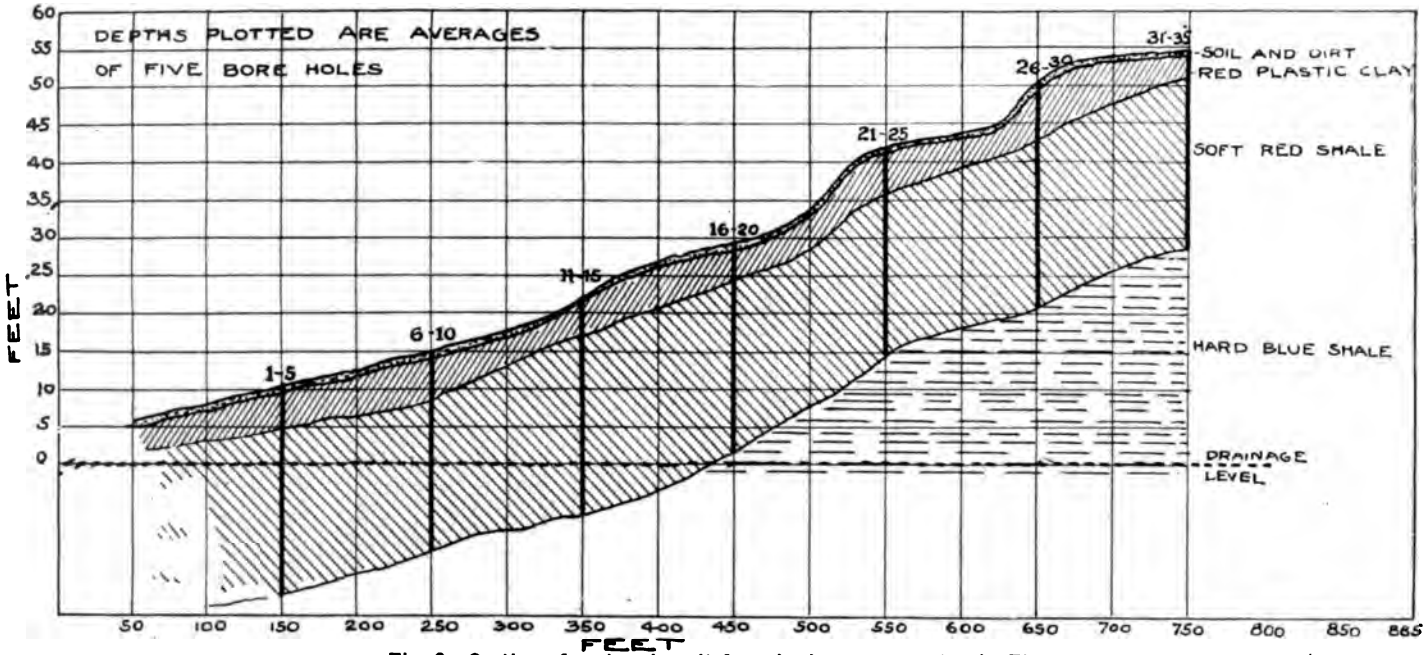

Fig. 8. Section of a clay deposit from borings represented in Figure 7.

The accompanying cuts illustrate this method of prospecting; the section shows the presence of soil, soft clay, soft red shale and hard blue shale.

Assuming that analysis has shown the soft red shale to be the most suitable and finding an average depth of 20 feet of this material, we evidently have available in each square of 50 feet, $50 \times 50 \times 20 = 50{,}000$ cubic feet of clay. But this procedure has not only shown the amount of clay available, but also the variations in composition, since two samples, are taken from a depth of 20 feet. This point should be well considered, as a knowledge of the composition of clays not only gives the prospective manufacturer accurate and valuable data, but is also of great help when manufacturing has been begun, since it tells the chemist what to expect in the future and may prevent some costly mistakes. When this is duly weighed, it surely ought to remove the last prejudice against the expenditure of the money necessary to carry on the preliminary survey.

METHOD OF DRILLING IN CLAY DEPOSITS.

In the prospecting of clay property, the samples required can be obtained either by digging down through the strata to be examined or by drilling holes. It is evident, of course, that by digging prospecting holes, the samples obtained will be large in amount and permit of sampling the deposit in the most thorough manner, and ultimately this must be done in every clay deposit even though only in, say, half a dozen places, at the extremities of the land available and in equal intervals between them. However, the cost of digging the holes is not inconsiderable and would not be resorted to until one is quite sure of his ground. Drilling, being so much cheaper, should be carried on during the preliminary survey, and it may be done as follows:

1. Boring with an auger. Applicable to clays which are free from stones and the softer grades of shales.
2. Drilling with the churn drill.
3. Combination of churn drill and auger.
4. Core drilling, with a serrated pipe, applicable to rather soft material only.
5. Core drilling with a pipe with sharpened edge at bottom, driven down.
6. Combination of churn drill and pipe drill.
7. Marl sampler, used in quite soft materials.

Auger.—The auger is the most successful implement in the exploiting of clay and shales and should be used much more extensively than it is. A good two-inch auger of best quality will answer in many cases.

Catlett* describes an auger which he has used in his prospecting work and which has given good service. The bit is made of steel or

*Trans. Am. Inst. Mining Eng., 1897.

Swedish iron with a steel point twisted into a spiral, with an ultimate diameter of 2 inches and a thickness of not less than one-fourth of an inch. The point is more effective when split. The auger proper should not be more than 13 inches long, having four turns. This was welded on to the end of 18 inches of one-inch wrought iron pipe, on which screws were cut for connection.

Churn Drill.—The churn drill, used universally in quarries and wherever hard rocks are to be penetrated, is a most effective tool. It is usually made as a heavy iron rod with a piece of steel at the end about 12 inches long, the cutting edge being about 2 inches. Its use is unnecessary in soft materials, but becomes imperative in hard rocks. In connection with the auger it forms a most useful combination, since it is used when going through hard rock and as soon as clay is reached the auger again becomes available. Such a drill was used by Mr.Catlett in connection with the auger described above. It was made of 1⅜-inch octagonal steel with a two-inch cutting face, which was likewise welded on to 18 inches of pipe cut for connections.

In addition other parts are found necessary: Ten feet of 1¼-inch iron pipe, threaded at either end for connection with one-inch pipe. When connected with one of the drill bits this becomes a jumper for starting holes through hard material. It is also used when desired to give aditional weight to the drill in going through rock. There are also needed sections of one-inch pipe and connections. An iron handle must be used with a total length of two feet, arranged with a central eye for sliding up and down the pipe and with a set-screw for fastening it at any point. Other accessories are a sand pump consisting of one or two feet of one-inch pipe with a simple leather valve and a string for raising or lowering it, two pairs of pipe tongs or two monkey pipe wrenches; as well as sundries: 25 feet of tape, oil can, flat file and a water bucket.

The auger is worked by two men, turning it by means of the handle, and enough water is used to soften the material. Usually the auger brings up some material which is dry and unaffected. Every few minutes as the auger becomes full it is lifted out, scraped off and put down again. The handle is moved up and tightened by means of the set screws as the auger goes down.

Auger and Drill.—When hard materials are encountered the auger bit is screwed off and the drill bit screwed on, thus forming a churn drill, which may be used for passing through the hard material, the auger being replaced as soon as the softer material is reached. The drill is used as seen in every quarry by being lifted and let fall, it being slightly turned at every stroke.

Mr. Catlett found that the best work was done on soft material, though no difficulty was experienced in going through hard rock. The cost increases materially at a depth of over 50 feet, but it is readily possible

to go down 80 feet and more. Down to 25 feet two men can operate it; from that to 50 feet a rough frame 15 to 20 feet is needed for the third man to stand on. Above 50 feet it is necesary to take off one or two of the top joints each time the auger or drill is lifted.

It is interesting to note Mr. Catlett's observations on drilling some holes, which might form a basis for the calculation of the approximate cost of drilling.

Record of Bore Hole.

	Feet.
Light yellow clay	14
Solid iron ore	3
Yellow clay	1
Solid ore	5.5
Yellow clay	1
White clay	1.5
	26

The above was put down by two men at work for six hours.

The following was put down by two men at work 15 hours and three men for 4 hours:

	Feet.
Red sand and sandstone	19
Yellow clay	3
Light yellow clay	8
Dark yellow clay	6
Black clay	2
Light yellow clay	2
Light yellow clay and black streaks	10
Light brown clay with white flint	2
	52

Serrated Pipe.—In place of the auger a pipe, provided at the end with sharp teeth, may be used, which is forced down into the soft material by twisting a two-foot handle. The sample will be a plug filling the pipe, representing the section of the length of the pipe. Another contrivance is a pipe with sharpened edges at the end, which is driven into the ground. In both samplers the plug of the material is, of course, forced out, another section of pipe connected with the first pipe and again started down. Both of them can be used more effectively in connection with a churn drill, which is able to cut through any hard material that may be met.

Whenever the material is very soft, as is the case with marl and marl clays, quite a number of devices are being used for doing this work and the most of them can be made by any mechanic without much trouble.

Hunt Sampler.—One sampler* offered on the market is that manufactured by Robert G. Hunt & Co., Chicago, Ill. It is a piece of steel tube about 18 inches long, slit longitudinally. The end entering the marl is capped and pointed with steel so that it will penetrate more easily. To the other end there is attached a longer or shorter rod, which can be turned by means of a handle. The two edges running lengthwise are sharp, so as to cut the marl. When the tool has been forced down to the depth desired it is turned half around, filling it with a clean swath of marl its whole length. Thus a perfect sample of the marl throughout the length of the sampler is obtained.

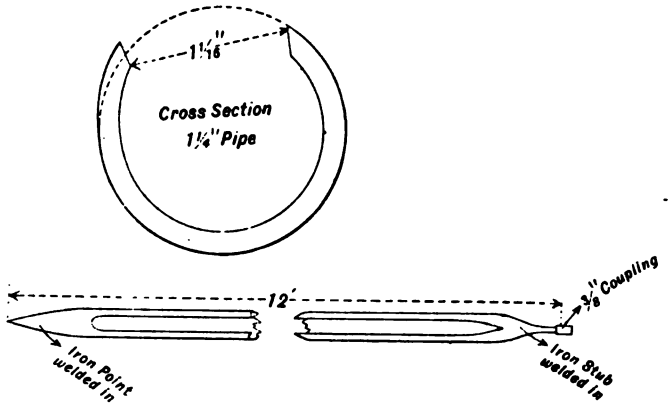

Fig. 9. The Hunt sampler.

Liquid Marl Sampler.—For marls almost in the liquid state the Geological Survey of Michigan used a modification of the Farr marl sampler.

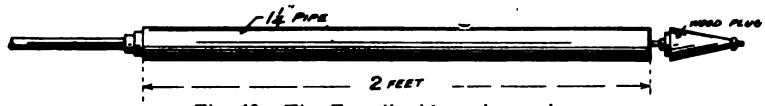

Fig. 10. The Farr liquid marl sampler.

The construction of this tool is readily understood from the diagram and it is used as follows:

The plug is first held firmly against the mouth of the pipe by means of the rod and the whole tool shoved down the desired length. Now the pipe is raised, holding the rod stationary, and is then shoved down to its former level, being forced tight against the shoulder of the plug. Both are now raised to the surface, the rod and plug removed and the sample taken from the pipe. A good sample can in this way be taken down to a depth of 18 feet. In order to cause the pipe to be forced down with greater ease it is best to sharpen the bottom edge.

*(Geological Survey of Michigan, Vol. VIII, Part III, page 12.
Marl and Its Application to the Manufacture of Portland Cement, D. J. Hale and Others.

SAMPLING LIMESTONE AND CEMENT ROCK.

In working with these harder rocks the churn drill is indispensable, it being worked either by hand or by power. In every case it will pay to obtain the service of a professional driller, such as are found in every district. At a comparatively small depth, drill holes are rapidly put through limestone material with a power drill.

If the rock to be sampled is in a quarry or other exposure, a vertical channel should be cut into the face, from top to bottom, sufficiently deep to remove all weathered rock, so that the sample obtained may be a true one. By drilling and the proper use of explosives such work can be carried on quite rapidly, but should in every case be done under the guidance of an experienced quarryman. For rapid work the diamond drill has given very good results.

In preparing samples for analytical work it goes without saying that great pains must be taken in order that they be average samples. Unless care is taken to do this, the entire work is of little or no value. The original sample should always be as large as possible and the entire quantity should be crushed together to 8 mesh and then intimately mixed and quartered down to about ten pounds. This should be again ground so that it will pass a 20 mesh sieve, and again quartered down until the amount for a laboratory test has been obtained, about 500 grams, which must then be put through a 100 mesh sieve. One cannot be too careful or painstaking in this preliminary work, as its thoroughness governs the value of all subsequent work.

The Ohio Geological Survey carried on the sampling as follows:

The samples came from the field in sacks, provided with pasteboard tags on the outside and wooden tags on the inside of each sack, the weight varying from 50 to 150 pounds. Wherever necessary the sample was dried on a hot plate dryer and then crushed by means of a small jaw crusher; usually the entire sample was run through in this manner, if the sample was a large one. The material was now thoroughly mixed, it being fine enough to pass through an 8 mesh screen. If the sample was less than 45 pounds, all of it was put into a specially designed dry ball-mill and of course in this case it was not necessary to mix it before putting in the mill. This machine, made of chilled cast iron, proved extremely valuable in this work, since it not only ground the 8 mesh material to any desired fineness, but at the same time it produced a sample almost ideal as to uniformity. The grinding was done by Greenland pebbles, which, of course, introduced some silica, but so small in amount that it could be safely neglected. In another part of this report the machine is described in detail. The usual charge of the mill was from 40 to 45 pounds. When a charge was ground the lid of the machine was removed and the flint balls, together with the ground material, dumped into a long box placed beneath the mill. From this box the whole charge was

shoveled onto a heavy screen consisting of iron rods, forming about an inch mesh. This screen, about 3 feet by 3 feet in size, was placed within a box 15 inches deep and 3 feet square on the inside, and it was let down into the box about 5 inches, so there was a space of about 10 inches depth beneath the screen. A smaller flat box was placed within the large box, under the screen, before the mill charge was shovelled onto the grating. The latter was just close enough to keep back the flint pebbles, while the ground material dropped into the box below. This was found to work very well, and it was a simple matter to prepare batches of limestone samples, or clay, or experimental cement mixtures. Clinker also was ground on this mill. In grinding clays or shales these must be thoroughly dry or the material will stick to the pebbles. In some cases it may even be necessary to apply a gas flame to the outside shell of the mill while it is running, to prevent the "pasteing" of the charge. The mill makes about 27 revolutions per minute and the power required to run it is quite trifling.

The samples thus obtained are thoroughly homogeneous and any portion of the ground mixture is a true average.

Though every laboratory is not in possession of such an outfit, similar mills, though small, may be constructed or bought with comparatively little expense. A small porcelain lined ball-mill driven by an electric or water motor will be found a valuable accessory of every technical laboratory.

CHEMICAL EXAMINATION OF CEMENT MATERIALS.

The chemical examination of the various substances entering into the domain of cement manufacture will be considered under the following topics:

1. Natural pozzuolane materials.
2. Slags, total analysis and sulphur determinations.
3. Natural cements.
4. Clay analysis.
5. Mineral analysis of clay, by the sulphuric acid method.
6. Mineral analysis of clay by heating with calcium carbonate.
7. Standard methods of limestone and cement analysis.
8. Commercial methods of cement material analysis.
9. Determination of insoluble residue in raw mixtures and Portland cements.
10. Physical supplementary methods.
11. Carbon determination and coal analysis.
12. Mechanical analysis of raw mixtures, clays and cements.
13. Special problems in cement chemistry.

CHEMICAL EXAMINATION OF POZZUOLANE MATERIALS.

Technical examination of natural pozzuolane, trass and similar hydrous materials.

1. From what we know of pozzuolane materials we realize that their hydraulic value depends on the amount of available silica present, that is, silica soluble partly in hot hydrochloric acid and completely soluble in a hot solution of sodium carbonate. A complete analysis is required in but few cases, and is of little value except where some irregular constituents are making their influence felt.

The complete analysis of a pozzuolane is carried on, as is customary for silicates, by fusion with sodium carbonate, separating the silica, alumina, iron, calcium oxide and magnesium oxide as is done for clays, the method of analysis of which will be given later on under the proper heading.

2. The soluble silica is determined as follows. Treat one gram of the sample with 40 cc. of hot dilute hydrochloric (1 : 2) acid in a casserole, boil for five minutes, dilute to 150 cc. with boiling distilled water and keep boiling for 15 minutes. Now filter the liquid off through a hardened filter, wash several times with hot water, and rinse any residue which got on the filter back into the casserole. To the residue now add 50 cc. of a solution containing 1 gram of caustic soda and 3 grams of sodium carbonate. Heat on a hot plate or water bath, for 60 minutes, but do not boil. Filter through the same hardened filter as before and return any residue transferred to the filter to the casserole. Add now 50 cc. of the alkaline solution, of half the strength given above, and heat for 30 minutes. Filter as before and repeat this treatment at least twice more, till no more flocculent silicic acid is detected in the filtrate on testing with ammonium chloride. Sometimes the test is rather slow to show. In this case make decidedly acid with hydrochloric acid and add in the test tube a few drops of ethyl alcohol. Cooling the hot test solution rapidly in water accelerates the reaction. To the residue in the casserole add 10 cc. of the hydrochloric acid, dilute to about 50 cc., heat to boiling, filter and wash almost free from chlorine with water containing about 10 per cent. of ammonium nitrate and a little alcohol. The total filtrate is now made distinctly acid with hydrochloric acid and evaporated to dryness in a porcelain or, preferably, a platinum dish. The residue is now heated in a hot air oven, best lined with clay tiles, at 120° C., till fumes of hydrochloric acid are no longer detected. Take up in a little hydrochloric acid, add boiling hot water and filter on an ashless filter. The filtrate is returned to the dish in which evaporation took place and is again boiled down to dryness and heated at 120° C., say for one hour. Take up again in acid and hot water, filter on same filter and wash practically free from chlorine. Ignite and weigh as silica, SiO_2. Final ignition must take place over a blast lamp. It is also advisable to test the purity of the silica with hydrofluoric acid.

The loss on ignition often is a valuable and sufficient criterion of the value of a puzzuolane material, it being due to the expulsion of the com-

bined water of the silicic acid. This simple method, of course, is applicable only to materials whose general composition is already known and can never be used as the sole method of comparing pozzuolanes.

ANALYSIS OF FURNACE SLAGS.

This method is quoted chiefly from "Notes on Metallurgical Analysis," by Professor N. W. Lord, professor of metallurgy and mineralogy at the Ohio State University and consulting chemist of the Ohio Geological Survey.

Weigh out one gram of the sample in a casserole, add 30 cc. of water and stir the slag to prevent caking. Now add 20 cc. of hydrochloric acid and heat. Everything should dissolve except a few flakes of silica and possibly a little carbon and sulphur. Evaporate to dryness and heat in the oven to a temperature between 110 and 120° C. till all of the acid is expelled. Take up residue in water and hydrochloric acid, filter off and transfer filtrate back to casserole for a second evaporation and heating. Take up in acid again as before, filter and wash. Ignite and weigh as silica. This residue is liable to contain traces of iron, titanium and spinel. It may be tested with hydrofluoric acid and any fixed residue deducted.

The alumina is now determined in the filtrate from the silica, to which a few drops of nitric acid have been added. In the absence of much manganese this can be done by precipitation with ammonium hydroxide, taking care to have plenty of ammonium chloride present and to redissolve the first precipitate, which is likely to contain a little lime. The precipitate is washed free from chlorine and then transferred to the filter. It may contain iron, phosphoric and titanic acid in the slag, but as these are rarely present in noticeable quantities they may be neglected. If the slag contains much manganese the alumina must be separated from it by a basic acetate precipitation. The precipitate is then redissolved in hydrochloric acid and the alumina now free from manganese is precipitated by ammonium hydroxide. This, however, is rarely necessary.

The presence of much manganese also influences the determination of calcium. If, hence, more than a few tenths per cent. of manganese is present add 2 or 3 cc. of ammonium sulphide to the filtrate from the alumina. Heat to boiling and boil for three minutes. Cool the liquid and transfer to a 500 cc. graduated flask; 250 cc. of this volume can now be measured out by filtering through a dry filter into 250 cc. graduated flask. In this solution, representing half of the sample, the calcium and magnesium can be determined gravimetrically or volumetrically.

If ammonium sulphide was used, add HCl to the filtered solution till neutral and then about 5 cc. in excess. Boil till the hydrogen sulphide is expelled, then add 0.5 gram of potassium chlorate and heat till the separated sulphur is dissolved. Now add ammonium hydroxide and pro-

ceed with the determination of the lime. Should a trace of manganese dioxide separate on adding the ammonium hydroxide, continue the heating till it dissolves and the solution is nearly colorless before precipitating the lime.

Determination of Sulphur in Slag.—The sulphur in slag is usually present as calcium sulphide. For the purpose of determination the sulphur may be brought to the condition of the sulphate in two ways, the dry or the wet method. The former is acomplished by careful fusion with alkaline carbonate, the latter by treatment with acid and oxidizing agents like bromine or chlorine.

Fusion Method.—Mix 1 gram of the finely pulverized slag with 6 grams of sodium carbonate and 0.5 to 1 gram of sodium nitrate, according to the amount of sulphur expected. Put the mixture in a platinum crucible. Put a heavy layer of sodium carbonate on top of the mixture and fuse carefully. As soon as it is well melted, chill the crucible by dipping the bottom into water. This will loosen the cake so that it can be removed.

The fusion must be made over an alcohol or gasoline lamp. Boil out the fusion in the water till all the material is soft and no hard lumps remain. If the solution is colored by $Na_2Mn_2O_8$ add a few drops of alcohol. Filter and wash well with hot water. Add HCl to the filtrate till just acid, evaporate it to dryness carefully and dry at 100° C. Now add 5 cc. of hydrochloric acid first diluted with its own volume of water. Warm and add 50 cc. of water, heating till everything is dissolved but a little SiO_2. Filter and wash. The filtrate should not exceed 100 cc. If it does, concentrate it. Now heat nearly to boiling and add 5 to 10 cc. of a 10 per cent. solution of barium chloride, previously diluted with 10 to 20 cc. of water and heated. Stir and let the precipitate of barium sulphate settle; when clear, filter, wash with hot water, ignite over Bunsen burner, cool, add one or two drops of sulphuric acid, ignite again and weigh the $BaSO_4$. Calculate the sulphur.

Wet Oxidation.—Place sample of 1 gram into a hard glass bulb provided with a three-hole rubber stopper. In one hole there is inserted a separatory funnel, through the second a tube connected to a Winkler absorption coil containing bromine, while through the third connection is made with an air supply tank, containing air under low pressure.

Bromine water is poured over the sample in bulb and hydrochloric acid is added slowly at intervals through the separatory funnel. The hydrogen sulphide evolved is oxidized largely by the bromine in the bulb, and any gas escaping is taken care of by the bromine water in the coil. During the reaction the bulb is shaken occasionally. When the decomposition is finished, heat to boiling and allow to cool slowly. The contents of the bulb and coil are now united, the excess of bromine is

driven off and the residue filtered off. The sulphuric acid is precipitated by means of barium chloride as given in the fusion method.

Volumetric Methods—In addition to the method of determining the sulphur as barium sulphate, we have several methods of determining the sulphur from *sulphides* volumetrically. The best known of these methods employs a standard iodine solution using starch as an indicator. It is extremely useful in the examination of blast furnace slags and is very rapid. (See N. W. Lord, "Notes on Metallurgical Analysis," p. 102.)

THE EXAMINATION OF NATURAL CEMENTS.

The analytical methods employed in the analysis of natural cements are practically the same as those used in analyzing limestones with the exception that fusion must be resorted to in order to bring about complete solution of the sample. .

Weigh out one gram of the finely ground sample and mix intimately on glazed paper with 3 grams of sodium carbonate. Transfer to a platinum crucible and raise slowly to a red heat over a Bunsen flame and after ten minutes, heat over the blast lamp for five minutes. Place crucible in casserole containing about 150 cc. of water, boil till mass has softened and has left the crucible, replenishing the water evaporated. Add hydrochloric acid till distinctly acid, keeping casserole covered with watch glass. Now add a few drops of nitric acid to solution and evaporate to dryness. The residue is heated at about 110° C. in a tile lined oven for one hour. After cooling, add 10 cc. of hydrochloric acid, let stand for a few minutes and dilute with boiling water. Filter and transfer filtrate back into casserole, evaporate to dryness as before and heat at 110° C. till all hydrochloric acid has been expelled. Take up again with 10 cc. hydrochloric acid, dilute with boiling water and filter through the filter used in the first separation of silica, thus adding any silica not separated in the first evaporation. In rapid technical work only one evaporation is made, but this never removes all of the silica present.

Now bring the filtrate to boiling and add ammonia to slight excess; boil for a few minutes and filter, washing several times with hot water. Remove funnel from above the filtrate and wash the precipitate of aluminum and ferric hydroxide into a clean beaker with hot water. Follow this by washing the filter with hot water containing 20 per cent. hydrochloric acid, allowing solution to run into the second beaker. Heat filtrate and precipitate in the fresh beaker till all of the iron and alumina is dissolved. Dilute, make slightly ammoniacal to reprecipitate the iron and alumina, boil for a minute and allow to settle. Decant clear liquid through the filter used before, taking care to wash it first with water containing a little ammonia.

The filter should be a 11 cm. ashless filter. Wash twice by decantation in this manner, using boiling hot water. If the precipitate is very

bulky, decant three times. Then transfer to the filter, wash, ignite and weigh as alumina and ferric oxide.

If it is desired to determine the ferric oxide in the material the quickest way of determining it is carried out as follows: Take two grams fuse with 6 grams of sodium carbonate and separate the silica as given above. After removal of the silica transfer the filtrate, acid with hydrochloric acid, to a 500 cc. flask and divide it into two portions, one of them being retained for the determination of the alumina and ferric oxide together, and of the calcium and magnesia; in the other half the iron is determined volumetrically by the bichromate method.

This is much more rapid than the solution of the ignited oxides of alumina and iron in potassium disulphate or sulphuric acid and titration with potassium permanganate. Of course for quick work, one gram may be used and this divided into two portions.

Heat the filtrate from the alumina and iron to boiling and add excess of a hot saturated solution of ammonium oxalate. Stir and allow to stand for five minutes. Filter off the supernatant clear liquid, and add boiling water to the precipitate remaining in the first beaker together with sufficient hydrochloric acid to redissolve the calcium oxalate. Raise again to boiling, add a little ammonium oxalate and make ammoniacal. Now allow the precipitated calcium oxalate to stand for one hour, filter and wash it, the filtrate being allowed to run into a fresh beaker. If in the first filtrate any precipitate is formed meanwhile, it must be filtered through the paper before the main precipitate is transferred.

The chief consideration in the calcium determination is that the work must be carried on as hot as possible, the solution and wash water being boiling hot. For very accurate work, the solution should stand for 12 hours in order to bring about complete precipitation of the lime. In rapid technical work, not more than ten minutes is allowed for standing, usually five. The difference between the five minute and 12 hours standing may be ½ per cent. If the work is done with boiling solutions the deficit is considerably less than this. In rapid work with rock low in magnesia, the re-solution and precipitation is not necessary, but cannot be avoided in the case of magnesian stone.

Ignite the precipitate of calcium oxalate over the blast lamp, cool, and add enough nitric acid to dissolve the oxide. Now add five or six drops of sulphuric acid and take the mass to dryness by heating gently with a Bunsen flame till the white fumes of sulphuric acid have ceased coming off. If no sulphuric acid fumes are seen, add more sulphuric acid and reheat. Then bring the residue to a dark red heat over the Bunsen flame and weigh it as calcium sulphate.

With a good blast lamp it is possible to ignite the calcium oxalate to the oxide and to weigh as such. In technical control work, the calcium is determined with sufficient accuracy volumetrically as described under the head of the examination of calcareous Portland cement material.

In the united filtrate from the calcium the magnesium is determined. Add to the cold liquid, 25 cc. of saturated solution of sodium diphosphate and excess of ammonia. The amount of solution should not exceed 400 cc. Stir thoroughly and let stand for 12 hours, especially when much magnesia oxide is present. Filter and wash with water containing about 10 per cent. of its volume of ammonia and some ammonium nitrate, about 100 grams to the liter. Dry and ignite the precipitate, which is magnesium pyrophosphate.

In examining natural cements it is sometimes necessary to determine the carbonates still present after burning, so as to obtain a numerical expression for the completeness of the burning. This is done by expelling the carbon dioxide with hydrochloric acid and absorbing the gas as usual in potash bulbs.

It may be desirable to make the determination of unburnt carbon in a natural cement. This is carried out with a sample treated with hydrochloric acid in order to decompose any carbonates present. After the acid treatment and expulsion of the free acid the sample is burnt in regular combustion tube, or a Shimer crucible, the carbon dioxide being absorbed in potash bulbs.

For rough approximation of the amount of water of hydration, carbon dioxide and carbon present in natural cements simple heating over the blast lamp will usually suffice.

COMPLETE ANALYSIS OF CLAY.

Fuse 1½ grams of the clay with 10 grams of sodium carbonate and separate the silica by double evaporation as given under the examination of natural cement. Test the weighed precipitate with hydrofluoric acid and any residue remaining, usually very small, should be considered as alumina. It is absolutely necessary to carry out the double evaporation, as without it no satisfactory results can be obtained. Filter the silica through a 11 cm. ashless filter. The evaporation should be done on a hot plate or asbestos stove. Frequent stirring during the pasty stage of evaporation is necessary.

The amount of silica obtained multiplied by 0.666 will give the silica in one gram.

Now transfer the filtrate from the silica determination to a flask calibrated to hold 600 cc. Retain of this volume 400 cc. for the determination of alumina and ferric oxide, lime and magnesia, and remove 200 cc. for the determination of iron by the bichromate method. The amount of iron found is of course multiplied by 2 to obtain the ferric oxide in one gram of sample. This procedure is much more rapid than the determination of iron by the permanganate method. If the latter is used, precipitate with ammonium hydroxide, the alumina and iron in the portion of 200 cc. which has been removed, decant the supernatant liquid and transfer the precipitate to the filter and wash it

with hot water. Now wash the hydroxides from the filter into a clean beaker and dissolve in dilute sulphuric acid. In the presence of titanium, reduce the iron with hydrogen sulphide, which must be expelled by boiling and by passing carbon dioxide through the liquid. Now titrate the solution of ferrous sulphate with potassium permanganate as usual. The use of hydrogen sulphide is especially necessary in the analysis of fire clays, where titanium oxide is never lacking and the iron content is very low, while for brick clays it is of little importance whether this is done or not. The bulky colloidal precipitate of aluminum and ferric hydroxide can only be washed sufficiently by decantation and water. This is provided for by arranging a large can, made of tin-lined copper, holding from 5 to 10 liters of water, at a considerable height above the laboratory table. This is kept gently boiling all the time and is supplied to the beakers or funnels by means of a long rubber tube provided at the end with a glass tube drawn out to a point and a pinch cock. This should be long enough to be swung from one end of the table to the other so that it may also be used for washing precipitates in place of the wash bottle. The tube can be counterbalanced by means of a weight running over a pulley.

The liquid to be decanted is best syphoned into an evaporating dish and kept boiling so that the volume may be reduced as quickly as possible to the desired volume. It is necessary to filter the concentrated washings in order to recover any small amounts of alumina and iron carried over.

In this as well as other industrial chemical work it is of extreme importance to watch closely the quality of the reagents used. It is best to frequently run blank determinations on each process so as to ascertain the exact amount of the impurities being brought in by the reagents used.

PROXIMATE OR MINERAL ANALYSIS OF CLAY

Repeated attention has been called to the mineral composition of clay, to its principal mineral constituents, clay substance, feldspar and quartz. The actual determination of these three constituents, according to Seger and Bischof, is carried out as follows:

Take one gram of the clay, transfer it to a casserole and add 50 cc. of sulphuric acid. Heat till white fumes begin to be given off and continue the heating for 8 hours. The volume must be kept up by the occasional addition of more sulphuric acid. After this heating cool the liquid and dilute with water to about 250 cc. Heat the diluted solution, and filter through a hardened filter and wash the precipitate, which has been transferred to the latter, with a hot solution of dilute hydrochloric acid (1:5) followed by washing with hot distilled water. Now carefully wash the precipitate back to the casserole and add 50 cc. of a solution containing 3 grams of sodium carbonate and ½ gram of caustic soda. Heat almost to boiling for 30 minutes, and decant through the same hardened filter. Wash any precipitate on filter back into casserole, into which pour 50 cc. of a solution

containing 3 grams of sodium carbonate and 0.1 gram of caustic soda. After heating the liquid, decant again through the same filter. Repeat until no more silicic acid is found in the filtrate. Usually four washings are sufficient. Then transfer the residue to the filter which has done service throughout this analysis and wash with hot water, acidulated with hydrochloric acid. Finally finish the washing with a 10 per cent. solution of ammonium nitrate. If the filtrate should become turbid, the addition of a little ethyl alcohol usually prevents the running through of the fine matter of the residue. Ignite and weigh the insoluble residue.

Mix the insoluble residue with eight times its weight of sodium carbonate, fuse and determine the silica as usual. In the filtrate from the silica precipitate the iron and alumina and weigh as in the regular analysis.

We can now calculate the amounts of clay substance, quartz and feldspar as follows: One gram minus the weight of the insoluble residue multiplied by 100 gives the per cent. of clay substance and all other minerals soluble in boiling sulphuric acid, like mica, hornblende, carbonates of iron or calcium, etc. The per cent. of silica in the insoluble residue minus 3.52 times the weight of the alumina and ferric oxide in the insoluble matter multiplied by 100 will give the per cent. of quartz, while the weight of the insoluble residue minus the weight of the quartz as just calculated times 100 will give the per cent. of feldspathic matter. The constant 3.52 is obtained from the typical analysis of orthclase feldspar and is equal to the ratio between the per cent. of silica and the per cent. of alumina, which are 64.76 and 18.4, respectively.

This method of analysis can make no claim to scientific exactness, but gives a close approximation to the actual mineral composition of white burning or kaolin-like clays. It does not give equally exact ideas, as to the constitution of the impure red-burning clays and shales, chiefly because the minerals taken into solution by sulphuric acid are numerous and the matter thus classified as clay substance, bears little resemblance to the constitution of real kaolinite.

This method, though giving extremely valuable data in regard to the mineralogical character of a clay, yet neglects to give expression to the coarseness or fineness of the grains composing the matter insoluble in acid, and hence fails to indicate the readiness with which the clay unites with lime to form silicates and aluminates. In order to overcome this to a certain extent, a mechanical analysis would have to be made of the insoluble residue, which, however, would still fail to tell just which of the various sizes are feldspar and which quartz. Lime can decompose and unite with the constituents of feldspar, the latter being a silicate, with far greater ease than with quartz, both being assumed to have the same size of grain. Hence we see that the ordinary rational analysis is deficient and does not produce exactly the kind of data desired.

MINERAL ANALYSIS OF CLAY BY HEATING WITH CALCIUM CARBONATE.

Lunge and Schochor proceed on an entirely different basis and make use of the fact, more akin to the purpose in view, that silicates are unlocked by being heated in contact with CaO, as is clearly shown by the J. Lawrence Smith method of alkali determination. These investigators, though they did not work with clays proper, but with marls, succeeded in showing that the CaO attacks most readily the combined silica and the silica present in a fine state of division, thus giving a direct expression of the cement-making value of the materials. By heating sufficiently, treating with hydrochloric acid and sodium carbonate the unlocked bases and the soluble silicic acid are removed, and the residue remaining is simply the matter which was not rendered soluble by the action of the CaO during the heating process.

The work by Messrs. Lunge and Schochor in regard to this investigation was very extensive, and before adopting their final method they made very thorough preliminary tests. The results obtained by them may be summed up as follows:

1. The solubility of raw marls in acid is not a sufficient criterion for determining their hydraulic value because acids are not proper reagents for determining unlocked silica, since silicic acid itself is soluble in acid only in proportion to the amount of chemical water contained by it. The acid treatment does not discriminate between coarse and fine silica, between amorphous silica and crystalline silica, nor between feldspar and silica.

2. However amorphous silica and quartz may differ otherwise, they show but little variation in behavior on burning with lime. The fineness of grinding is far more important. Although with the same degree of fineness and the same mode of mixing with equal amounts of CaO and heating under similar conditions, amorphous silica gives rise to a higher percentage of soluble silica than the quartz or a mixture of the two kinds of acid, yet when ground sufficiently fine, even pure quartz is acted upon almost completely and much more so than amorphous silica not so fine, but still extremely fine from the ordinary standpoint. Since the activity of silicic acid depends upon its contents of chemical water, after ignition it does not differ from so much quartz.

3. Chemically combined silica is completely unlocked. No matter how fine free silica is, it is always attacked less than silica in combination and hence it is shown that the best source of silica for cement purposes is a silicate, as far as transportation of the silica to the lime is concerned.

Lunge and Schochor have thus indicated a way by means of which it is possible to determine the per cent. of chemically active material in a marl, to separate the combined and very fine silica from the coarser quartz, thus permitting the statement that the higher the per cent. of silicate and very fine quartz is in a clay the higher is the value of the latter for hydraulic purposes. In other words, the higher the per cent. of dissolved

material after heating with CaO and treating with HCl and Na_2CO_3 the higher is the value of the clay for hydraulic cements.

The method of working adopted by the two investigators named was as follows:

Samples of marl were taken, in the shape of lumps of walnut size which were heated in a gas furnace to a temperature of about 1100° C. without pulverizing or mixing, for two hours. These burned samples were pulverized, treated with HCl and Na_2CO_3 the residue being weighed after thorough washing. The value of the respective marls was expressed inversely by the per cent. of residue.

In order to prove that these tests really stand for expressions of the hydraulic value of the marls, Lunge and Schochor proceeded to grind the materials and to make cements of them by burning to vitrification and grinding the resulting clinker. The burning was done in a small test kiln. The hydraulic cements thus produced were subjected to the usual cement tests, which proved strikingly that for the marls examined, the hydraulic value was a function of the solubility of the clayey constituents when treated as mentioned above.

Upon studying the results obtained by Lunge and Schochor, Prof. Edward Orton, Jr., suggested the use of this method for the testing of clays in regard to their suitability for cement manufacture. The investigators just named restricted their method to marls, and although it is extremely valuable for the determination of the hydraulic value of any one marl, yet its results are not generally applicable and must always be restricted to this class of material. The factors in this method are evidently the variables of the clay substance, coarse and fine quartz, coarse and fine feldspathic matter, and in addition to this the lime contents. This evidently may in some cases give rise to conflicting results, as for instance, when there are two marls to be examined of which one has a coarser grain of sand, but a higher content of lime than the second marl, which is fine grained and has a higher percentage of combined silica but a lower per cent. of lime. The method now suggested for clays adopts a constant amount of lime, thus eliminating one variable.

The identity of structure which Lunge and Schochor are so careful to preserve by burning the materials in lumps is not interfered with by reducing them, *without grinding*, to the size of a 40 mesh sieve. In fact by burning the materials in lumps the outside factor of irregularity due to natural formation is so great as to introduce an additional source of error. For a product as homogeneous as cement the consideration of the bed structure is entirely unnecessary.

Thus the process of the Ohio Geological Survey is intended to determine the hydraulic factor of a clay by reducing the latter without grinding, with the assistance of water, so that it will pass through a 40 mesh sieve, care being taken not to reject the coarser material left on the sieve nor to break up any particles by grinding. When in the state

of a slurry, lime is added in the shape of precipitated calcium carbonate and thoroughly stirred with the clay. This mass is now dried down and rubbed through a 40 mesh sieve, mixed thoroughly on a sheet of glazed paper by means of spatula and burned in a furnace. A weighed amount of the ignited mixture is treated with hot hydrochloric acid for five hours, filtered and washed, and the residue is digested with a 10 per cent. solution of sodium carbonate with heating, until no more flocculent silica is observed on testing with ammonium chloride.

The Lunge and Schochor method and that of the Ohio Geological Survey differ in the following respects:

1. The above named investigators restrict their method to marls, while the Survey extends it to the testing of all clays.

2. The former work with the natural materials, having varying percentages of lime, while the latter maintains a constant amount of lime by adding the lime lacking, in the form of pure calcium carbonate and also having the lime present in excess.

3. Lunge and Schochor ignite the materials in the shape of lumps taken from the deposit; the Survey reduces them so that the soft portion will pass through a 40 mesh sieve with the aid of water and accomplishing the mixture of clay and lime when the former is in the condition of a slurry.

Experimental Work in Demonstration of the Value of the Process.—Having thus outlined the method of working, there now remains to prove that it really gives expression to a co-efficient which is consistent with actual results in the manufacture of cement. For this purpose it was decided to bring the method as nearly possible to uniform conditions of operation and to agree upon a method of mixing, burning and analysis.

The description of the work done naturally falls under the following headings:

1. Sampling and preparation.
2. Mixing.
3. Burning.

Sampling and Preparation.—The clays arrived at the laboratory of the Ohio State University Ceramic Department in sacks, in the shape in which they were sent by the field collector. These clays, according to their nature, were treated in different ways. Clays of the soft, alluvial type, after being put through an 8 mesh sieve and repeatedly quartered according to the quantity on hand, were dried at 100° C., and about 500 g. was reserved for the analysis, being run, as far as possible, through a 40 mesh sieve and thoroughly mixed; the coarser portion, of course, being added to the finer. When the material was a hard shale, it was necessary to crush it and pass it through an 8 mesh sieve. A quantity of the reduced shale was then heated at 100° C. till perfectly dry and then allowed

to soak in water for 24 hours. If this was not sufficient, boiling was resorted to, which was kept up for 6 to 8 hours, if necessary. The mass was then evaporated to dryness and rubbed through a 40 mesh sieve. For very hard material, rubbing with a rubber pestle may be permitted.

Mixing.—The sample was now ready to be mixed with the lime. This was done by weighing out about 25 grams of the clay to be examined, whose gross analysis must be known, stirring it up with water to a thin slip and adding reprecipitated calcium carbonate. This mixture was stirred thoroughly, evaporated to dryness, rubbed through a 20 mesh sieve and thoroughly mixed with a spatula.

At this stage of the work it was necessary to determine the proper amount of lime to be added to a clay so as to attain the object sought, that is, the decomposition of the clay substance proper and the formation of a lime silicate, without running into danger of fusing the resulting mixture at the temperature employed in heating. In order to accomplish this a series of test-mixtures was made, employing a very fine-grained, soft clay, with little bonding power, which is used in the manufacture of Portland cement, at Harper, Ohio. The clay has the following analysis:

SiO_2	50.70
$Al_2O_3+Fe_2O_3$	17.00
$CaCO_3$	16.80
$MgCO_3$	9.80

The clay by itself was made the start of the series and the lime was increased as shown by the following table. The mixtures were burned at a temperature of 1100° C., this heat being maintained for 75 minutes. The mixtures of clay and calcium carbonate were made up into briquettes weighing about 75 grams, with the aid of water, placed upon a biscuit plate and burned in the small furnace used for this purpose.

No.	Per cent. of Calcium Carbonate.	Per cent. Residue.	Remarks.
1	16.8	....	Clay alone.
2	25.	....	
3	30.	....	
4	35.	....	More or less completely fused.
5	40.	....	
6	45.	....	
7	50.	....	
8	55.	....	Vitrified.
9	60.	3.55	Quite hard.
10	65.	....	Hard.
11	75.	1.12	Soft, but somewhat too hard for easy reduction.
12	80.	2.16	Soft.
13	85.	3.00	Soft and friable.

No. 11 of the table must be considered doubtful, an error having certainly been made in the analytical work. The results of the table show that

it is essential to have at least 75 per cent. of calcium carbonate present in the mixture, not so much because less lime might not unlock the silicate or not attack the free silica, but owing to the fact that the resulting mass after burning becomes hard and stone-like and hence inconvenient for reduction. For this reason it was decided to use a standard mixture of 80 per cent. $CaCO_3$ and 20 per cent. of the clay be tested, which results in a friable mass easily reduced. This amount of lime also allows for a sufficient excess, so that uniformity is obtained as far as the reagent is concerned.

In the determination of the insoluble residue of these mixtures sufficient material was taken to correspond to two grams of the clay. In this and other series the total lime was determined volumetrically in a number of analyses. This was done in order to express the per cent. of residue in terms of the actual weight of clay taken, thus making due allowance for the lime introduced as reagent, since the mixing of clay and lime can never be so intimate as to make it permissible to weigh out any amount of the mixture and obtain the actual amount of clay taken by calculation, depending upon the per cent. of calcium carbonate originally added under the supposition that the mixture is perfect. Later on this method was modified in such a way that 2 grams of the dried clay were weighed out, transferred to a beaker and made up into slip with water. To this was added the amount of lime corresponding to the required proportion of 1 part of clay to 4 of calcium carbonate. The mixture was carefully transferred to a porcelain crucible, evaporated to dryness, mixed on a sheet of glazed paper with the spatula and returned to the crucible in which the sample was burned, being covered with a lid. In this way, of course, the determination of limes becomes unnecessary.

The analysis proper is carried out by taking the sample, treating with hydrochloric acid (1:3), allowing it to boil for five minutes till in solution. This liquid is now filtered and washed nearly free from chlorine, the residue being washed back into the casserole and treated with the alkali solution as indicated under the head of rational clay analysis till no more silicic acid is found in filtrate. The residue is then treated with hydrochloric acid (1:4) washed free from chlorine, ignited and weighed.

The main precaution to be observed is to keep the work as hot as possible, while yet allowing the silicic acid to settle. The use of long stemmed funnels is to be preferred to suction flasks.

Burning.—For burning the mixture, there was available a dental furnace manufactured by the American Gas Furnace Co. which was intended to be fired with gasoline vapor, but which was modified so as to burn ordinary kerosene. For this purpose a ¼ inch pipe was introduced into the lower cylindrical part of the furnace. The pipe was run to a can fastened to the wall and was fed with oil from the reservoir by

means of a stop cock and funnel. The oil dripped into the open furnace making a sight feed arrangement. The blast was furnished by a positive rotary blower through a ¾ inch pipe.

The mode of operating the furnace was as follows: At the bottom of the cylinder beneath the furnace proper there was placed a small shallow iron pan into which the oil dripped from the feed pipe and which served as an evaporator for the oil. When ready for operation a small bunch of waste saturated with oil was placed upon the pan, ignited and covered with a few pieces of wood and charcoal. Upon this small charge of fuel there were now placed pieces of fire brick, the size of a large walnut, which filled up the cylinder completely and served the purpose of offering resistance to the passage of gases and air, thus mixing them for proper combustion. The air was blown in through three small tuyeres distributed around the cylinder. As soon as the charcoal was fully ignited, the kerosene was allowed to flow slowly and a weak blast maintained. Gradually the flow of oil and the blast were increased, until the maximum supply was reached.

Before the supply of oil had begun, a fire clay tile was placed across the furnace occupying the space formerly taken up by the muffle. Upon this tile were placed the crucibles or biscuit saucers carrying the samples to be ignited. At the same time a porcelain tube containing the platinum wire and thermo-couple of a Chatelier pyrometer was placed in position, just touching the mixtures to be heated.

The rise in temperature was readily followed by means of the pyrometer whose millivolt meter is set up in a closet at a distance of about 7 feet from the furnace.

The question now arose in regard to the temperature to be employed in the burning. It was at once evident that the work to be accomplished by the heat is two-fold.

First, the carbonic acid must be expelled from the calcium carbonate.

Second, the silicate must be decomposed and the finely divided silica converted into lime silicate, soluble in acid.

The first function obviously fixes the lowest limit of the temperature to be employed. From the work done by Prof. Hertzfeld, we know that at a temperature of 1050° C. the carbonic acid is completely expelled. Lunge and Schochor employed a temperature between 1060° and 1120° Centigrade, their statements being in this respect not as definite as could be desired. However, from the extensive knowledge in existence in regard to the unlocking of silicates by the J. Lawrence Smith process, we know that it is not necessary to carry the temperature very high and this is also not desirable owing to other considerations. The heating must not be carried so high that silicates and aluminates analogous to those of hydraulic cements are formed, reactions which are entirely uncalled for in this process, and which might result in the crystallization of compounds.

of different solubilities. We thus have the limits of temperature fixed, the lower one being that of the complete expulsion of carbonic acid and the higher one being that of the formation of hydraulic silicates and aluminates.

It was not thought necessary, in view of the knowledge available, to undertake an extended series of experiments as to the temperature required. But it was decided to heat a mixture of clay and carbonate of lime at different temperatures and to observe at what temperature the residue becomes constant. For this purpose a marl, from Harper, Ohio, was selected, whose composition is as follows:

	Per cents.
SiO_2	8.75
$Al_2O_3+Fe_2O_3$	2.78
$CaCO_3$	79.22
$MgCO_3$	2.67

A sample of this material was heated to 1000°, 1050°, 1100° and 1150° C. with the results as shown by the following figures, the time chosen being 90 minutes, that is, the respective temperature was maintained for this time. The amount of marl taken for analysis was 2 grams.

Temperature	1,000°	1,050°	1,100°	1,150°
Residue	2.06	1.00	0.4	.....

The results were found to check sufficiently close in other burns. The samples were made up into briquettes.

It is thus seen that practically all the marl was decomposed at 1100°. Although this series might have been extended to mixtures of clay and carbonate of lime, yet the fact that this marl, which is acknowledged to be a most excellent cement material, was practically decomposed, together with the data obtained from the work of Lunge and Schochor, Hertzfeld, Smith, seems sufficient to warrant the acceptance of this temperature as the standard.

The question of the time of heating was one that next needed attention. In order to determine the factor of time, the same marl was used and heated for 30, 60, 75, 90 and 120 minutes at the temperature of 1100° C. with the following results:

Time, minutes	30	60	75	90	120
Residue, per cents	8.6	1.28	0.4	1.0	0.55

In spite of the irregularity in the 90-minute burn, which shows an increase of 0.6 per cent. of the residue, it was decided to adopt 75 minutes as the standard length of the rational burn. The irregularity may be explained as one of the variations necessarily coincident with all rational analyses of this kind, which do not work upon finely pulverized, homogeneous samples.

By 75 minutes is meant the time during which the sample is exposed to the temperature of 1100° C., which of course means a much longer burn, since one hour elapses before the furnace can be raised to 1100°.

There can be little doubt but that the time thus allowed is ample to accomplish the intended result. It is well known that for the complete decomposition of silicates in the alkali determination, a heating of 50 minutes over a Bunsen burner is sufficient, the temperature of which certainly does not exceed 1100°.

Having thus arrived at standard conditions of burning which, in the nature of the case, are bound to be more or less arbitrary, it was decided to apply this method to typical constituents of clay, prepared in several well-graded sizes. For, by knowing the action of lime upon each of these materials and for each of the several sizes of grain, it is possible for us to obtain a more definite idea of the character of the more inert constituents of clay, not readily available for hydraulic purposes. Of course, we can say in general that as particles of quartz feldspathic and micaceous minerals are coarser, the more resistant will they prove to the action of lime, yet we do not know just to what extent the chemical action of lime is affected by the size of grain.

For this reason two series of experiments were carried out in which quartz and feldspar grains were burned together with lime in a mixture containing 80 per cent. of the calcium carbonate, the heat being maintained for 75 minutes at a temperature of 1100° C.

The quartz taken for this purpose was pure quartzite which was crushed and graded to the sizes by sieving. Six sizes were adopted, as follows:

1. Grains between 150 and 120 mesh sieve.
2. Grains between 120 and 100 mesh sieve.
3. Grains between 100 and 80 mesh sieve.
4. Grains between 80 and 60 mesh sieve.
5. Grains between 60 and 40 mesh sieve.
6. Grains between 40 and 20 mesh sieve.

In addition to these sizes, there was included in the series a ground flint, as sold to potters, which is quartzite ground to a fine powder in ball-mills using flint pebbles.

After being mixed with $CaCO_3$ in the condition of a slip, the mixtures were evaporated to dryness and made into briquettes which were burned.

On making the rational analysis the results obtained were as shown in the following table:

Sizes.	Ground flint.	150-120	120-100	100-80	80-60	60-40	40-20
Per cent. residue.....	28.83	63.8	78.53	86.52	86.27	93.78	96.83
Per cent. taken in solution.....	71.17	36.2	21.47	13.48	13.73	6.22	3.17

This table shows quite strikingly the effect of size of grain upon the action of lime, and brings out two kinds of facts which have a direct bearing upon the cement industry.

It confirms the general statement that the coarser the grain, the smaller the effect of the lime. Free silica contained in clay, unless very fine, finer than that passing through a 150 mesh sieve, is rendered available only after thorough grinding, which means a certain extra amount of wear and tear of machinery, and a decrease in efficiency corresponding with the coarseness of the quartz.

The second fact is to a certain extent opposite in character to the first. It tells us that it is commercially possible to reduce free quartz to a fineness in which it is available for combination with lime. To be more clear, it may be said that of two clays available, one high in alumina and low in quartz, and one with a proper alumina content, but rather high in free silica, the results in regard to the quality of cement will certainly be better when the silicious material is used, in spite of the fact that its grinding is more difficult.

The tendency, only too common, is to work softer clays, which often bring in more alumina, and result in a tendency to "hot" cements, which must be toned down by gypsum. Granted that the presence of quartz makes it necessary to grind longer, yet the clay should not altogether be chosen with regard to its easy reduction, but also in regard to the ultimate quality of the cement.

Similarly to the quartz series, the same process was carried through with the corresponding sizes of feldspar grains, which were obtained from several fine specimens of orthoclase crystals, that apparently had not been kaolinized perceptibly.

Sizes.	Ground Feldspar.	150–120	120–100	100–80	80–60	60–40	40–20
Per cent. residue.....	3.75	15.45	31.00	64.29	79.63	95.72	.....
Per cent. taken in solution.....	96.25	84.55	69.00	35.71	20.37	4.28	.....

These results show at once the great difference between quartz and feldspar in regard to being acted upon by lime. It becomes evident that feldspar is a desirable constituent of cement materials. Light-burning clays high in feldspar should therefore receive more attention with reference to the manufacture of light-colored cement.

In addition to these series, commercial potter's kaolin of a good grade was treated by the same process, resulting in a residue of 3.07 per cent., 96.93 per cent. being taken into solution. This verifies the work of the German investigators, who found that clay substance was easily unlocked by lime.

Finally a synthetic mixture, having the following composition, was prepared with the intention of closely imitating such a clay as is commonly found in the alluvial or glacial clays of the country, and as is likely to be tried as a source of silica and alumina in cement manufacture.

	Per cent.
Commercial washed kaolin	50
Feldspar, 150–120 mesh	10
Feldspar, 120–100 mesh	10
Quartz, 150–120 mesh	10
Quartz, 100–80 mesh	10
Quartz, 60–40 mesh	10
	100

This mixture would have on analysis a composition roughly as follows:

	Per cents.
SiO_2	65.50
Al_2O_3	24.00
K_2O	3.00
H_2O	7.50
	100.00

Upon being heated with lime it showed, on analysis, a residue of 31.36 per cent., 68.64 per cent. having been taken into solution. The residue, calculated from the previous experiments, should be 30.72 per cent., which is a practical check on the previous work.

The foregoing method has yet to be subjected to the wide test of practical application. Not until it is demonstrated that the clays which this method condemns, are also condemned after actual use as cement materials, and that clays which this method endorses as good, are actually found good in use, can it be treated as an established and valuable thing.

However, its claims to usefulness rest on broad and secure technical reasoning. No one can successfully dispute that clays, which give up their silica most readily to the action of lime, are, other things being equal, the best for making cements. Neither can any one affirm that any other method yet proposed or used, has been successful in showing any close relation between the amount of sandy minerals in a clay and its value to the cement-maker.

The clay must contain other sources of silica than that of kaolinite, if it is to be serviceable to the cement-maker, and, in addition, these sources must be such as will readily yield it up. The older methods have stopped after showing that the requisite silicate matter is present. This proposed method is designed to go one step farther, in showing not only

that it is present quantitatively, but also whether it is qualitatively suitable as well. It shows whether the silicate matter which is present, is in a form in which it will be readily assimilated into the calcium silicates to be formed, or whether it is in such physically unfit condition that only a limited part of it will be useful.

In the latter case, using the data furnished by the older methods, the cement-maker is likely to produce a cement too poor in combined silica. Or, if he recognizes this danger, and uses an excess of clay to bring the proportion of available silica up to the proper point, he runs into the counter difficulty of bringing in too much alumina.

This method of analysis enables us, therefore, to discriminate between clays as to their cement making value. An ideal clay when heated with calcium carbonate and treated with hydrochloric acid and sodium carbonate solution should show practically no insoluble residue, and as a rough approximation it might be said that no clay considered for cement making purposes should contain more than 10 per cent. insoluble residue. If, hence, a clay has the proper alumina-silica ratio and shows a small insoluble residue without extremely fine grinding it may be said to be entirely suitable for cement manufacture. Likewise, this method furnishes a most excellent guide as to the fine grinding of the raw materials, that is, how long a given mixture must be ground in order to show complete solution which is equivalent to perfect chemical activity. On the other hand it shows also when we are grinding a mixture too long, that is, when we are expending unnecessary power on this operation.

The heating of the clay-calcium carbonate mixture may be done over any good blast lamp.

ANALYSIS OF CALCAREOUS MATERIALS.

In this connection we must clearly distinguish between the accurate academic methods of analysis and the rapid methods practiced by the factory chemist which lack more or less in accuracy. Owing to the various modifications of methods employed in cement practice the results obtained by the various chemists must show considerable variation. The Society of Chemical Industry has endeavored to systématize analytical methods pertaining to the analysis of calcareous materials and its committee has proposed the following tentative method,* as suggested by Mr. Clifford Richardson and modified by Mr. W. F. Hillebrand for the analysis of limestones, raw cement mixtures and Portland cement:

EXACT METHODS.

Solution.—One-half gram of finely powdered substance is weighed out and, if a limestone or underburnt mixture, strongly ignited in a platinum crucible over the blast lamp for 15 minutes. It is then transferred

*Report of the Subcommittee on Uniformity in Analysis of Materials for the Portland Cement Industry. *Jour. Society Chemical Industry*, No. 1, 1902.

to an evaporating dish, preferably platinum, covered with a watch glass and 10 cc. hydrochloric acid diluted with about 50 cc. of water added. Digestion on the water bath is allowed to go on for about 15 minutes, when the substances should be entirely decomposed. The cover glass is then removed, washed and the solution evaporated to dryness on the water bath.

Silica.—The residue without further heating is treated at first with 5 to 10 cc. strong hydrochloric acid and then as much water as the dish will hold.

The cover is replaced and digestion allowed to go on for 10 minutes on the bath, after which the solution is filtered and the separated silica washed thoroughly with hot water. The filtrate is again evaporated to dryness, the residue without further heating taken up with acid and water and the small amount of silica it contains separated on another filter paper. The papers containing the residue are transferred to a weighed platinum crucible, dried, ignited first over a Bunsen until the carbon is completely consumed and finally over a blast for 30 minutes and checked by further blasting of 10 minutes or to constant weight. The silica, if great accuracy is desired, is treated in the crucible with about 10 cc. hydrofluoric acid and 4 drops of sulphuric acid and evaporated over a low flame to complete dryness. The small residue is washed, blasted, cooled and weighed. The difference between this weight and the weight previously obtained is the amount of silica. Any considerable amount of insoluble residue must be fused with sodium carbonate and the silica separated as before, the filtrate being added to the main filtrate. One evaporation for the dehydration of the silicic acid, however, is only required.

Alumina and Iron.—The filtrate, about 250 cc., from the second evaporation for silica, is made alkaline with ammonium hydroxide and boiled to expel excess of ammonia or until there is but a faint odor of it. The precipitated iron and aluminum hydroxides after settling are washed once by decantation and slightly on the filter. Setting aside the filtrate the precipitate is dissolved in hot hydrochloric acid, the solution passing into the beaker in which the precipitation was made. The alumina and iron are then reprecipitated by ammonium hydroxide and the second precipitate is collected and washed on the same filter used in the first instance. The filter must, however, first be moistened with dilute ammonia. The filter paper with the precipitate is then placed in a weighed platinum crucible, the paper burnt off and the precipitate ignited, and finally blasted over the lamp for 10 minutes, being careful to prevent reduction. After cooling it is weighed as alumina and ferric oxide, which also contains the small amounts of titanium, phosphorus and manganese present.

Ferric Oxide.—The combined ferric oxide and alumina precipitate is fused in a platinum crucible at a very low temperature with about 10

grams of potassium acid sulphate, the melt taken up with hot water and 25 cc. dilute sulphuric acid. The clear solution is then digested on the steam bath for about 10 minutes, and if great accuracy is desired the small amount of silica filtered off, weighed and corrected with hydrofluoric acid and sulphuric acid. The filtrate is reduced by hydrogen sulphide, boiling out the excess afterwards while passing carbon dioxide through the flask, and titrated with potassium permanganate. This procedure eliminates the influence of titanium.

Lime.—To the combined filtrate from the alumina and ferric oxide a few drops of ammonium hydroxide are added and the solution brought to boiling. To the boiling solution 20 cc. of a saturated solution of ammonium oxalate is added and the boiling continued until the calcium oxalate appears as a well defined granular precipitate. It is allowed to stand for 20 minutes or until the precipitate has settled and then filtered. The precipitate and filter are placed, wet, in a platinum crucible and the paper burnt off over a small Bunsen flame. It is then ignited, redissolved in hydrochloric acid and the solution made up to about 100 cc. with water. Ammonia is added in slight excess and the liquid boiled. The small amount of alumina which is separated is filtered and weighed, and the amount added to that found in the first determination, when great accuracy is desired. The lime is then reprecipitated by ammonium oxalate, allowed to stand until settled, washed, weighed as oxide by ignition and blasting to constant weight or determined with a standard potassium permanganate solution, which method, however, is somewhat questionable as to accuracy.

Magnesia.—The combined filtrates from the calcium precipitate are acidified with hydrochloric acid and concentrated on the steam bath to about 150 cc. 30 cc. of a saturated solution of $Na(NH_4)HPO_4$ are added and the solution boiled for several minutes. It is then removed and cooled by placing the beaker in ice water. After cooling ammonia is added, drop by drop, until the crystalline ammonium magnesium orthophosphate begins to form, and then in slight excess with constant stirring. It is then set aside for several hours in a cool atmosphere and filtered. The precipitate is redissolved in hot hydrochloric acid, the solution made up to about 100 cc., 2 cc. of a saturated microcosmic salt solution added and ammonia, drop by drop, with constant stirring until the precipitate is again formed as described. Allow to stand for about two hours, when it is filtered on paper or in a Gooch crucible, cooled and weighed as magnesium phosphate.

Alkalies.—These are determined by the J. L. Smith method, with or without addition of calcium carbonate to the ammonium chloride.

Sulphur Tri-Oxide (SO_3).—One gram of cement is dissolved in 15 cc. of hydrochloric acid, filtered, and the residue washed thoroughly;

evaporation to dryness is unnecessary. The solution is made up to 250 cc. in a beaker and boiled. To the boiling solution 10 cc. of a saturated solution of barium chloride is added slowly, drop by drop, and the boiling continued until the precipitate is well formed. It is then set aside over night, filtered, ignited and weighed as barium sulphate.

Total Sulphur.—One gram of the material is weighed out in a large platinum crucible and fused with sodium carbonate and a little potassium nitrate over a gasoline or alcohol blast lamp. The melt is treated in a crucible with boiling water and the liquid poured into a tall narrow beaker and more hot water added until the mass is dissolved.. The solution is then filtered.

The filtrate contained in a No. 4 beaker is acidulated with hydrochloric acid, made up to about 250 cc. with distilled water, boiled, the sulphur precipitated with barium chloride as barium sulphate and allowed to stand over night.

Loss on Ignition.—One-half gram of cement is weighed out in a platinum crucible and blasted for 15 minutes. The loss, which is checked by a second blasting, is the loss on ignition.

RAPID OR FACTORY LABORATORY METHODS.

In the laboratories of the cement industry the determination of calcium oxide is, of course, the principal part of the routine work and a number of rapid methods for its determination as well as for the estimation of magnesia have been worked out. These methods are as follows:

1. Titration of the oxalic acid from the washed precipitate of calcium oxalate, decomposed by acid.
2. Titration by the use of standard acid and alkali solutions.
3. Volumetric determination of the carbon dioxide evolved from the calcium carbonate.
4. Volumetric determination of magnesia depending on the fact that magnesia is entirely precipitated from a strongly ammoniacal solution, as magnesium ammonium arsenate by addition of sodium arsenate. The arsenic is determined volumetrically and the magnesium calculated from it.*

Method 1.—In American practice the first method is used most commonly and seems to enjoy the greatest favor among cement chemists. It requires a potassium permanganate solution of such strength that 1 cc.= 0.005 gram calcium carbonate or calcium oxide, depending on whether a raw mixture or burnt cement is to be analyzed. The method is carried out for limestone as follows:

Weigh out 0.5 gram of the finely ground sample into a platinum crucible and ignite over the Bunsen burner to destroy all organic matter.

*"*R. K. Meade, The Chemical and Physical Examination of Portland Cement,"* p. 42.

Transfer the sample to a 300 cc. beaker, add 30 cc. of water, cover with a watch glass, add 10 cc. of hydrochloric acid and a little nitric acid. Boil till all the soluble matter is dissolved and all the carbon dioxide expelled. Wash off watch glass and dilute to about 150 cc. with water previously boiled. Add ammonia slightly in excess and heat to boiling. If the insoluble residue is low and it is not desired to weigh the insoluble matter it is not necessary to filter it off. The calcium oxalate is precipitated in the boiling hot solution as usual by the addition of 40 cc. of a hot solution consisting of 20 cc. of concentrated ammonium oxalate solution and 20 cc. of water. Stir for several minutes and let settle for five minutes.

Decant the supernatant solution through an ashless filter, add 40 cc. of hot water, decant, add another portion of hot water and decant for the third time. Now transfer the precipitate to the filter and wash three or four times with hot water. To determine whether or not the precipitate has been washed sufficiently, catch a few cc. of the last filtrate on a watch glass, add a drop of sulphuric and one drop of potassium permanganate solution. If the liquid shows a strong red color the washing is finished, if the color is discharged further washing is necessary. The calcium oxalate is now washed back into the beaker in which it was precipitated, using hot water and diluted to about 200 cc. if necessary. Place the beaker under the funnel and run through the filter into the beaker 30 cc. of dilute sulphuric acid (1 volume of acid to 3 of water). Wash the filter thoroughly with hot water and stir the contents of the beaker while running in the acid. Heat liquid to about 80° C. and titrate with the permanganate solution to a faint pink color which should not disappear for two minutes.

The potassium permanganate solution should not be standardized against iron or ammonium ferrous sulphate, but against calcite checked repeatedly by the gravimetric method of calcium determination.

R. K. Meade* proposes to keep the iron and alumina in solution by the addition of 5 per cent. oxalic acid, the calcium being precipitated by ammonium oxalate and determined volumetrically with a standard permanganate solution. The results have been found by Meade to be very satisfactory.

Method 2.—The acid alkali methods, owing to their rapidity and simplicity, are frequently made use of, but great caution is necessary in their use, and the results should be carefully checked gravimetrically from time to time owing to the fact that these methods are subject to errors. Larger amounts of alumina and iron influence the results most decidedly. S. B. Newberry** proposes the following working method:

Prepare a n/5 solution of hydrochloric acid and a n/5 caustic soda solution, standardizing with pure Iceland spar, which has been analyzed

* "*Cement and Engineering News*," June, 1903.
** "*Ibid*," March, 1903.

gravimetrically. One-half gram of pure spar should exactly neutralize 50 cc. of acid.

Weigh out ½ gram of a finely ground limestone, transfer to an Erlenmeyer flask of about 500 cc. capacity provided with a rubber stopper and a thin glass tube 30 inches long, to serve as a condenser. Run into the flask 60 cc. of the 1-5 normal acid, attach the condenser and boil gently, allowing no steam to escape from tube, for about two minutes. Wash down the tube into the flask with a little water. Remove the condenser and cool the solution thoroughly by immersing the flask in cold water. When quite cold add five to six drops of phenol-phthalein solution (1 gram in 200 cc. alcohol) and titrate back to first pink color with 1-5 normal caustic soda solution. It is important to recognize the point at which the first pink color appears throughout the solution, even though this may fade in a few seconds. If the alkali be added to a permanent and strong red color the lime will come too low. The amount of acid used is called the first acid and the alkali used to titrate back, the first alkali.

In case the materials contain a very small amount of magnesia the operation ends here and the calculation is simply: Number cc. acid minus number of cc. alkali multiplied by 2×0.56=per cent. calcium oxide. In this case it is unnecessary to cool the solution, and a permanent red is obtained at the point of neutralization.

The determination of magnesia proceeds as follows:

Transfer the neutral solution to a large test tube 12 inches long and 1 inch inside diameter marked at 100 cc. Heat to boiling and add 1-5 normal caustic soda solution, about one cc. at a time, boiling for a moment after each addition until a deep red color is obtained which does not pale on boiling.

This point can be easily recognized within one-half cc. after a little practice. Note the number of cc. soda solution added to the neutral solution as second alkali. Dilute to 100 cc., boil for a moment and set the tube aside to allow the precipitate to settle. When settled take out 50 cc. of the clear liquid by means of a pipette and titrate back to colorless with 1-5 normal acid. Multiply by 2 the number of cc. of acid required to neutralize and note as second acid.

Calculation:

Second alkali: second acid$\times2\times0.40$=per cent magnesia. First acid$\times$(1st alkali+2nd alkali—second acid)$\times2\times0.56$=per cent. calcium oxide.

Method 3.—The volumetric determination of carbon dioxide from calcium carbonate, though used to some considerable extent in Europe, has not found favor among American cement chemists, who prefer other volumetric methods. The Cramer-Baur burette is one of the most convenient apparatus for this purpose.

Magnesia.—Prof. N. W. Lord determines magnesia volumetrically by precipitating as magnesium ammonium phosphate, filtering, washing, treating with 1-10 normal sulphuric acid and titrating back with 1-10 normal ammonia, using cochineal indicator.

Ludlow and Harrop Method.—In order to illustrate actual laboratory practice the methods employed at two cement works are given, the first one being used at the works of the National Portland Cement Company, Durham, Canada, having been worked out by Mr. S. H. Ludlow, chief chemist, and Mr. Carl B. Harrop, assistant chemist. Mr. Ludlow has kindly sent the following account of the method:

RAPID METHOD OF RUNNING PORTLAND CEMENT MIXTURES.

The following methods of determining the amount of clay to be added to a given measured quantity of marl in the wet state to produce a correct slurry are based upon the relations existing between the weight and volume of a cubic yard and a cubic centimeter of water.

Required to find the number of pounds of clay to be added to a cu. yd. of marl of any composition or consistency. Take such a volume of the marl that the weight of the total solids in the volume taken, expressed in milligrams, will represent pounds per cu. yd. By a familiar course of reasoning, similar to that employed in establishing the assay ton, the following proportion may be deduced:

Original volume : part taken : : mass represented : part of represented mass taken as unit in analysis.

Let A = Original volume.

Let B = Mass represented or one pound.

Let 1 = Part of represented mass taken as a unit in analysis, or one mgm.

Let X = Part of original volume taken or number of cc. required, so that each mgm. will equal pounds per cu. yd.

Substituting—

$$A : X :: B : 1$$

1 cu. yd. = 764500 cc. (or gram of water).

1 lb. = 453593 mgm.

Therefore, A = 764500 cc.

B = 453593 mgm.

Substituting and solving for X,

$$764500 : X : : 453593 : 1$$

$$X = 1.685 \text{ cc.}$$

Hence if 1.685 cc. of water (standard conditions) is taken, each mgm. equals 1 pound in the cu. yd. Obviously this will apply to any liquid of whatever density or to a homogeneous mixture of solids and liquids or a thoroughly agitated sample of marl in the semi-liquid state.

Therefore, if 1.685 cc. of marl be evaporated to dryness, in a tared dish, and weighed, its weight expressed in miligrams equals the number of pounds of marl per cu. yd. The weight of marl in a given volume being known, the amount of clay to be added may be readily calculated from the composition of the marl and clay, and the desired composition of the slurry.

Several applications of this principle may be made according to the uniformity of the marl, the system of mixing in the mill and the facilities for correction of slurry, should occasion demand.

METHOD No. 1.

As 1.685 cc. is too small a volume of marl to measure with sufficient accuracy, measure ten times that quantity in a hard glass tube about 95 mm. high by 15 mm. in diameter, calibrated to contain exactly 16.85 cc. Wash into a tared tin or nickel dish, with the jet from wash bottle, using as little water as possible, evaporate to dryness, cool quickly and weigh. For greater accuracy take three samples from top, bottom and center, respectively, of the marl tank and take the average weight of the three samples. Grind the dried samples intimately in an agate mortar. Take two portions, each one-tenth the weight of the dried samples. One portion is analyzed for $CaCO_3$ by the acid-alkali method. For this purpose ½nHCL and ½nKOH solutions are the most convenient. The value of one cc of the HCl solution in terms of per cent. of $CaCO_3$ (or mgms. $CaCO_3$) should be accurately determined by running a number of average samples of the particular marl in use, a complete analysis having been previously made in each case by a standard method. This standardization of the solution with the marl to be used is very essential as the ease with which the acid attacks other constituents of the marl besides the $CaCO_3$ varies considerably in different marls. In the second portion of the dried sample the clay matter is determined by precipitating the silica, alumina and iron together, with ammonia and eliminating their combined weight in the usual way.

We now have a number of pounds of clay matter and of calcium carbonate in each cu. yd. of the tank marl.

Let A = Pounds of $CaCO_3$.
B = Pounds of clay matter.
C = Factor representing pounds $CaCO_3$ required to satisfy one pound of clay matter in the marl.
D = Factor representing number of pounds of $CaCO_3$ required for each pound of clay to be used.
X = No. lbs. clay required per cu. yd. of marl.

Solve for X by the following formula:

$$\frac{A-(B\times C)}{D} = X.$$

METHOD No. 2.

To avoid the necessity of determining the clay matter in the marl, first make a number of preliminary analyses of the particular marl bed to be worked to determine the combined per cent. of calcium carbonate, silica, alumina and iron in an average sample of marl. From samples of tank to be analyzed take as before, samples of 16.85 cc. each, evaporate to dryness in a tared dish, cool and weigh. One tenth the number of milligrams in the dry sample equals pounds of marl per cu. yd. Take 1 gm. for analysis and determine by ½nHCl and ½nKOH solution (standardized as in method No. 1) the per cent. of $CaCO_3$ (or CaO as desired.)

Let A = Pounds of marl per cu. yd.
B = Per cent. of $CaCO_3$ in marl.
a = Combined per cent. of clay matter and $CaCO_3$ as previously determined to be the average of marl used.
C = Factor representing number lbs. $CaCO_3$ required for one lb. of clay matter in marl.
D = Factor representing number of lbs. of $CaCO_3$ required for one pound clay used.
X = Pounds of clay required per cu. yd of marl.

Solve for X by the following formula:

$$\frac{(A\times B)-C\times(a-B)\times A}{D} = X.$$

By practice the analyst is able to discriminate between the clay matter and organic matter in the flask during the period of boiling with the acid solution and after titratting back with the alkali solution, and the per cent. of clay can be judged with sufficient accuracy after the percentage of $CaCO_3$ has been determined. In doubtful cases where the marl shows unusual irregularity in $CaCO_3$, the contents of the flask may be thrown on the filter and the clay matter quickly determined by ignition. This, however, is seldom found necessary.

METHOD No. 3.

From each of several samples taken from different parts of the tank marl, take a small sample, say 20 cc., measured in a wide tube. Introduce into a dry 6-inch porcelain mortar, no water being used in transferring from the tube to the mortar. Grind the marl to an impalpable condition when the mass should be absolutely homogeneous. From this take for analysis 3.37 cc. (=2×1,685 cc.) this being a sufficient quantity when properly manipulated and requiring a convenient quantity of ½nHCl for analysis. This can best be accomplished by the use of a pipette constructed according to accompanying cut. The pipette should be carefully dried before filling with marl and the marl all carefully removed with a jet of water. ½nHCl and ½nKOH solutions standardized as in method No. 1 are employed for analysis, 50 cc. of the HCl solution being used for a determination. By the use of a table expressing the value of any number of cc. of HCl solution (the number of cc. liable to be used being determined by trial) in terms of milligrams of $CaCO_3$, the number of pounds of $CaCO_3$ is read direct.

Example.—If each cc. HCl is found to equal 2.435 per cent. $CaCO_3$ in 1 gram=24.35 mgms. $CaCO_3$ and we find that 3.37 cc. marl requires 45 cc. HCl, then 24.35×45= 1095.71 mg.

1095.71÷2=547.8 pounds $CaCO_3$ per cu. yd. of marl. The amount of clay to be added is figured by the aid of the formula employed in method No. 1.

$$\frac{A-(B\times C)}{D}=X.$$

B may be determined on an average sample as in method No. 2, or in case of irregularity of marl the contents of the flask are thrown on the filter, ignited and weighed. We have thus the pounds of $CaCO_3$ and of clay matter per cu. yd. and proceed with the calculation of clay matter required as in method No. 1, though not always so accurately as method No. 1 and 2. This last method is especially advantageous because of the rapidity of manipulation, 20 minutes being sufficient for analysis and calculation of results. When the marl is sufficiently uniform and the plant is so arranged as to admit of the proper correction when necessary, remarkable uniformity may be obtained with a minimum of time and labor.

The above methods have all been found to give excellent satisfaction in cement practice, having been used according to the condition to which each was best suited in various cement plants in the United States and Canada.

Fisher's Method.—The following working method is used by Mr. Fred Fisher, chemist of the Newaygo Portland Cement Company. In employing this method Mr. Fisher has succeeded in completing, without help, eight analyses in an eleven hour shift, besides doing other routine work, but the ordinary procedure is to make seven exact analyses of slurry in 24 hours, employing, of course, a night assistant.

PREPARATION OF THE SAMPLE.

About a quart of the wet mixture or slurry, taken from a well-agitated tank, is brought to the laboratory. It is passed through a sausage grinder. This breaks up

any shells or other lumps and helps to insure a homogeneous sample. About 50 or 60 cc. are poured out thin on a hot electric griddle, where it dries in a few moments. The dry sample is ground fine in a mortar without sifting.

DRYNESS.

A small wide-mouth bottle is filled with the slurry and leveled off. About 20 cc. is poured into a tared pan, in which it is dried on the hot plate and then weighed. The bottle, without being cleaned, is filled with water from a burette, indicating the amount of sample taken. From this and the weight, as above, a factor is obtained with which to calculate the amount of material in a measuring tank. "Weight" divided by "burette reading" equals "dryness," which multiplied by the capacity of the tank in litres would give the number of kilos of dry material.

ANALYSIS.

0.5 g. of the sample and 5 g. sodium carbonate are mixed in a thirty cc. platinum crucible and fused over a blast lamp. After the charge is melted it is poured out on a

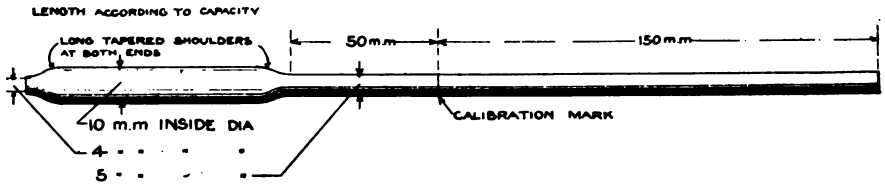

Fig. 11. The Ludlow and Harrop marl pipette, to contain 3.37 c.c.

clean carbon plate. With the aid of a dropper the crucible and cover are cleaned and rinsed with a minimum of 1 to 1 hydrochloric acid, into a No. 6 evaporating dish. The lump of fused material is dropped in and about 15 seconds later 10 cc. of concentrated hydrochloric acid is added, the dish is covered with a watch glass and set on a water bath. After all effervescence has ceased and it has steamed a moment, to automatically rinse any spattering from the covering, the latter is removed and set aside to be used later. With this minimum amount of liquid the fused mass is all decomposed, but part of the sodium chloride and most of the silica is precipitated by the strong acid. This precipitate being dense and granular stays at the bottom of the dish, and the evaporation proceeds more rapidly than usual, without scumming over or caking, and is finished in twenty to thirty minutes; when especially hurried the evaporation is hastened by playing on the surface of the liquid with a Bunsen flame.

When entirely free from smell of acid the dish is removed from the water bath. After wetting the saline mass with hot water, 10 cc. concentrated hydrochloric acid is added, the sides of the dish washed down with hot water, covered with the watch glass and set on the hot plate to boil a moment. With the aid of the filter pump and bell jar the solution is filtered into a 600 cc. Griffin beaker through an 11 cm. ashless filter. The dish is rinsed out with hot water and the filter washed twice. The funnel with the filter is transferred to a filtering flask, the dish cleaned out with the aid of a finger cot and rinsed into the filter, and the latter washed twice more. By the above procedure practically all the soluble part of the sample is in solution, and its volume kept low. The filter is burned and ignited over the blast lamp, and the silica transferred from the platinum crucible to a tared watch glass and weighed.

To the filtrate are added a couple of drops of strong bromine water and 20 cc. of a mixture of ammonia and ammonium chloride. This mixture is of such a degree of strength that the above amount will contain ammonia enough to neutralize the 10 cc. of

DETERMINATION OF CARBON AND COAL ANALYSIS.

This determination is best made by means of the usual carbon train or the Shimer crucible. Though the carbon determination is hardly ever necessary for the raw materials, it will give useful data in regard to the carbon left unburned in the cement.

The ultimate analysis of coal is made in very few, if any, cement works but an occasional proximate analysis, determining the volatile combustible matter, the fixed carbon, moisture and ash, is very necessary. The question of the ash from coal is too much neglected in American cement practice; its influence upon the cement composition is very marked in some instances. The subject of the effect of the ash upon the cement should be carefully studied by every cement chemist for his particular cement and coal. For this purpose it is necessary, of course, to analyze the ash, which is done by treating it like clay, fusing with sodium carbonate, and separating the silica, alumina, ferric oxide, lime and magnesia as usual.

It need hardly be emphasized that the amount of sulphur in coal should receive careful consideration. With the present rapid methods of analysis available, there is no excuse for neglecting this important determination. An admirable method of rapid sulphur determination has been worked out by J. D. Pennock and D. A. Morton in the laboratory of the Solvay Process Co.*

ANALYSIS OF THE KILN GASES.

The most faithful representation of what takes place in a furnace of any kind is given by the analysis of the gases as they flow into the stack. It gives an accurate record of just what efficiency has been attained, whether too much or not enough air has been admitted. And yet our cement mills seem to ignore this valuable aid entirely, and do not seem to care to know whether or not they are exercising fuel economy. In some cases on record it is evident that from 10 to 35 per cent. or more fuel is being wasted which might be saved. The writer is not now speaking of the losses inherent in the present rotary kiln, but losses due simply to excess of air in burning.

Gas analysis is easily carried out by means of the well-known Orsat apparatus, requiring but little time and trouble. By means of a pipe system (⅜-inch pipe) and a water syphon, samples of gas may be drawn continuously from any particular kiln, and the analysis carried on in the laboratory, or by means of a portable sampler, easily and cheaply made from gas piping. The contrivance may be set up at a kiln, the desired number of samples drawn and then taken to another kiln. The sample is drawn through a ¾-inch pipe projecting from 2 to 4 feet into the upper end of the rotary kiln, the pipe being plugged at the end and

*Journal American Chemical Society, December, 1903.

perforated for about 12 inches. It is obvious that the pipe should not be too close to the circumference of the kiln in order not to be hit by any lumps of material which might cling to the kiln lining. Of course there is little danger of this where a dry mixture is used. The pipe should be rinsed with a solution of borax which will produce a kind of glaze on the inside. If possible it is run straight out through the brickwork of the stack; outside of the kiln the ¾-inch pipe reduces to ⅜ inch. Of course, a pipe system connected to every kiln and permitting of sampling the gas from any particular kiln simply by turning on the water syphon in the laboratory is most convenient, but is by no means necessary. This is especially true since, after the proper rate of feeding the coal and blowing in of the air have been established on the basis of gas analysis, but very few analyses may be necessary. Needless to say, all the pipe fittings must be made as air-tight as possible.

Owing to the familiarity of the Orsat apparatus a description of it and the simple mode of operating it are unnecessary. With practice a gas analysis can be made in a very short time (about 15 minutes). A detailed description of the working of this instrument, together with the mode of sampling, etc., is found in Lord's Metallurgical Notes, and other books on metallurgical or gas analysis.

In calculating the per cent. of air corresponding to the gas analysis in question we must remember that the composition of the waste gases from a lime or cement kiln shows an excess of carbon dioxide, due to the decomposition of the calcium carbonate. Any calculation, therefore, depending solely upon the carbon dioxide content shown by the analysis is bound to be erroneous. In order to show the relations existing between the air admitted and the per cent. by volume of carbon dioxide, oxygen and nitrogen given by the analysis, a short discussion of the principles governing the evolution of gases from the fuel will be found advisable.

If the fuel used were pure carbon and no carbon dioxide from other sources could mingle with the gases the composition of the waste gases would invariably be 79 per cent. by volume of nitrogen and 21 per cent. of carbon dioxide, provided complete combustion took place, and no excess of air was admitted. If excess of air was admitted the sum of the per cent. of carbon dioxide and oxygen would be practically equal to the constant value, 21. But coal contains besides carbon, hydrogen (hydrocarbons) which also consume oxygen, so that the per cent. of carbon dioxide is correspondingly decreased. The one constant factor in the gas analysis is furnished by the nitrogen, which undergoes no change, being chemically inert, and hence it furnishes the most reliable basis for the calculation of the air admitted in the combustion of the fuel. The proportion of the nitrogen present in the air to the oxygen content of the latter is invariably in the ratio of 79:21, by volume, or for every volume

of oxygen we have 3.76 volumes of nitrogen. If, now, we let N be the total per cent of nitrogen found by analysis and O the per cent of oxygen determined, the amount of nitrogen, n_1, corresponding to the amount of air really made useful in the combustion must be equal to N—n, or, making

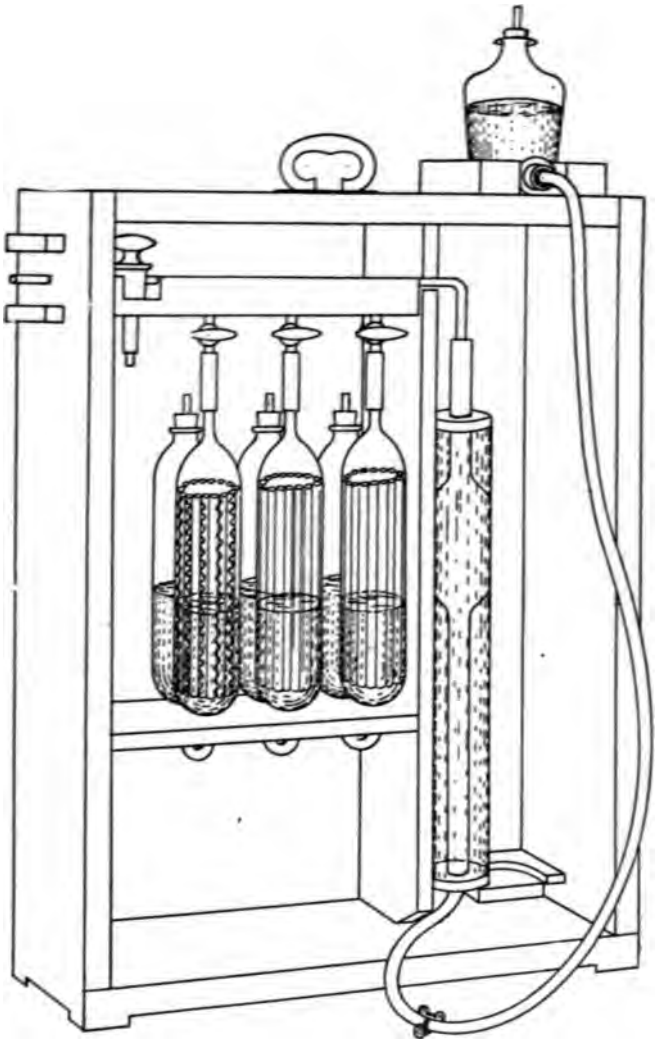

Fig. 12. The Orsat apparatus for gas analysis.

use of the per cent. of oxygen found, $n_1=N-3.76O$. Thus, without calculating the amount of air itself, we can obtain the ratio between the air introduced and the air used by making use of the ratio of nitrogen brought in and the nitrogen of the air really deprived of its oxygen, which is the same thing as if we compared the volumes of air proper.

In this manner the ratio of total and useful air is obtained by the expression $N \div (N-3.76O)$. We can readily convert this into per cent.

by volume by multiplying the numerator by 100, making the expression $100N \div (N-3.76O)$. We must remember that N here is always the per cent. by volume of nitrogen as found by the gas analysis, and O the per cent. of oxygen. The resulting expression is a value either above or below 100, depending on whether the conditions of firing are oxidizing or reducing. For theoretically perfect conditions, that is, when only just enough air is admitted to burn the fuel, no oxygen is shown by the analysis, and hence the ratio is $100N \div N$ or 100. Therefore 100 per cent. of air is the ideal towards which all in charge of purely heat producing furnaces must strive. If, for example, a ratio of 160 per cent. is shown by the above calculation, it tells that an excess of 60 per cent. of air has been admitted.

On the other hand, an amount of air lower than 100 per cent. stands for a deficit of air proportional to the lack of oxygen. Such an analysis shows but little oxygen, and indicates the presence of combustible gases, especially of CO. Any amount of combustible gases present will thus stand for minus oxygen, so that the formula becomes $100N \div [N-(-3.76O)]$ or $100.N \div N + 3.76O$.

To illustrate, a gas analysis shows the following composition by volume:

Carbon dioxide,	14.3 per cent.
Carbon monoxide,	4.1 per cent.
Oxygen,	0.2 per cent.
Nitrogen.	79.8 per cent.

To calculate the amount of air entering the furnaces. Carbon monoxide represents an unburnt gas consuming for complete combustion one-half its volume of additional oxygen, or $4.1 \div 2 = 2.05$ volumes of oxygen, which is necessarily minus in sign. But as the analysis shows 0.2 per cent. of free oxygen the minus oxygen will be $2.05 - 0.2 = 1.85$ per cent. Substituting in the formula we have, $100 \times 79.80. \div 79.80 + (3.76 \times 1.85) =$ 91.9 per cent. of air admitted, or the deficit of air as shown by this analysis is 8.1 per cent. These simple calculations are the ones most commonly required in the examination of the firing conditions of boilers and kilns, and all the data for it are furnished by the Orsat apparatus. More complicated and accurate apparatus, while important for scientific research, is unnecessary in practice, though the Elliot apparatus may be used to determine the hydrocarbons without difficulty.

In some investigations it is desirable to know just what part of the oxygen of the air is used for converting the carbon of the coal to carbon dioxide, and what part burns the hydrogen of the coal to steam. This calculation is illustrated by the following example. Assuming that the coal used contains

83.75 per cent. carbon
4.13 per cent. hydrogen
2.68 per cent. oxygen.

we find that the available hydrogen is $4.13-\frac{2.68}{8}=3.80$ per cent.

Now 83.75 parts by weight of carbon require $\frac{32}{12}\times 83.75=223.32$ parts of oxygen, while the hydrogen requires $3.8\times 8=30.40$ parts of oxygen, the total parts by weight of oxygen for 100 parts of the coal being thus $223.32-30.40=253.72$. Since the air contains 21 per cent. by volume of oxygen there are used for the combustion of the carbon.

$$\frac{21\times 223.32}{253.72}=18.49 \text{ volumes of oxygen.}$$

The hydrogen requires

$$\frac{21\times 30.4}{253.72}=2.52 \text{ volumes of oxygen.}$$

But every volume of oxygen on combustion furnishes one volume of carbon dioxide; therefore on using the above coal the ratio of the carbon dioxide to the nitrogen must be 18.49:79.

In the burning of cement, where a considerable amount of the fire gases is made up of carbon dioxide from the decomposition of the calcium carbonate, it may be desirable to know the amount of the CO_2 present in the gases resulting from the limestone. Knowing the total amount of carbon dioxide shown by the analysis we can calculate the amount of this gas due to the combustion alone from the percentage of air represented by the analysis as calculated from the expression, $100N\div N-3.760$.

If we let the per cent. of air be equal to a, and assuming that a coal is used of the composition given above, the carbon dioxide produced in the combustion must be obtained by the expression $79:18.49=\frac{N.a}{100}:X$ or $X=\frac{N.a\times 18.49.}{100\times 79}$ If, for example, the nitrogen found by the analysis is 69 per cent., the air used=95 per cent. and the carbon dioxide=30 per cent. the CO_2 produced by combustion must be: $\frac{69\times 95\times 18.49}{100\times 79}=15.34$ per cent. and the carbon dioxide evolved from the limestone must be $30-15.34=14.66$ per cent.

MECHANICAL ANALYSIS OF RAW MIXTURES AND CEMENTS.

Sieve Analysis.—The fineness of grain of the mineral constituents of a clay governs to a large extent its chemical activity, and hence it becomes an important and interesting problem to bring about a separation of the various sizes of grain. The simplest and most obvious method of separation is the sieve analysis, in which the material to be examined is passed either in a dry or wet state through a series of sieves. The usual combination for a sieve analysis as practiced in the laboratory of

the Ohio Geological Survey comprises the 20, 40, 60, 80, 100, 120, 150 and 200 mesh sieves, these being small copper frame affairs conical in shape, 3¼ inches in diameter at the top and 2¼ inches at the bottom. These sieves are readily put together, telescope-like in a vertical arrangement, so that the coarsest sieve, No. 20, is at the top, the finest at the bottom. By making a weighed amount of materials up into a thin slurry with water, using, say, 10 grams, the separation is effected by pouring the liquid mixture through the top sieve, washing out the beaker and playing a fine stream of water from a water bottle on the sieve until no more can be washed through. It is then placed on a watch glass and dried in a laboratory drying oven. When dry and cooled the sieve and its contents are weighed. The weight of the dry sieve alone has been previously determined. The difference between the gross and the net weights of the sieve will, of course, give the weight of the residue. Similarly, the weights of the residues on the remaining sieves are determined readily and quickly.

If it is desired to make a sieve analysis of a cement, water evidently cannot be used, but it is necessary to work with alcohol, redistilled over caustic lime. The separation is effected just as in the case of the clay mixtures.

Analysis by Sedimentation.—For the separation of grains passing through the 200 mesh sieve we must employ another means of differentiation. Two principles are commonly used in the classifying of fine particles, suspension and elutriation.

The first is obviously the simplest mode of separation, the practical difficulties being in securing perfect separation of the particles, in preventing flocculation and in avoiding currents. The particles may be prevented to a large extent from flocculation by boiling and the addition of a little ammonia.

In regard to the theory governing the fall of small grains while in suspension in a liquid, Rittinger has given a formula, the equation of a parabola, which expresses the relation between the velocity in meters, V, the diameter of the particles, D, and the specific gravity, d, for average particles as follows:

$$\frac{V}{D} = 2.44(d-1)$$

Wagoner, on the other hand, has found that the parabolic formula does not apply, but has derived a formula for fine grains expressing the relation between the diameter and rate of fall, viz.:

$$V = c\frac{D^{3/2}}{\sqrt{aD^2+b}}$$

where V is the velocity in mm. per second; D is the diameter of the particle in mm. and a, b and c are constants.

For quartz with a specific gravity of 2.64, c=100.4, a=0.903 and c=0.5195.

R. H. Richards[1] gives the following values for the velocity of the fall of quartz for various coarser diameters:

Diameter in mm.....	0.16	0.22	0.33	0.51	0.81	1.36
Velocity in mm. per second...	32	45.2	64.0	90.5	128	181

A satisfactory method of carrying out this sedimentary analysis is given by Osborn,[2] who makes three separations of particles ranging from 0.25 to 0.05 mm., 0.05 to 0.01 mm. and from 0.01 mm. diameter to fine dust. He uses a sample of 30 grams and passes the material through sieves. For carrying out the work he simply places the sieved material into a beaker, adding water and allowing the sediment to settle a short time.

"The turbid liquid is then decanted from the sediment and after standing until a slight deposit has formed is again decanted and the sediment examined with a microscope. If sand (0.25 to 0.05 mm.) is present, the subsidence of the turbid liquid is continued until no more sand is deposited. As the sand subsides rapidly there is no difficulty in altogether freeing the liquid first decanted from this grade of particles. The sediment thus obtained contains all the sand, a part of the dust (0.01 mm. and finer) and much silt (0.05 to 0.01 mm.). As only dust and the finest silt render the water turbid, the sediment is stirred a few times with a fresh quantity of water and decanted after standing long enough to let the sand settle. When the water is decanted free from turbidity, the last portions passing through the sieve with clear water are added to the sediment and the decantation continued so as to remove most of the silt. When no more silt can be easily removed from the sediment without decanting sand, the decantations are made into a different vessel and the subsidence so timed as to remove as much of the silt as possible.

"By using a little care at least three-quarters of the sand are thus obtained free from silt. The rest of the sand is mixed with the greater part of the silt, which has been decanted into the second vessel. The size of the smallest particles in this vessel is determined with the microscope, to make sure that its contents are free from dust, as they usually will be if, after settling for a few moments, they leave the water free from turbidity.

"The material is thus separated into three portions, one containing sand, one sand and silt, and the other silt, dust and impalpable powder,

[1] *Ore Dressing*, p. 469.
[2] *H. W. Wiley, Agricultural Analysis*, p. 196.

clay. The sand and silt are separated from each other by repeating the subsidences and decantations in the manner just described.

"In this way there is removed from the sediment, on the one hand, a portion of silt free from sand and dust, and, on the other hand, a portion of sand free from silt; then is obtained a second intermediate portion consisting of sand and silt, but less in amount than the first and containing particles of diameters much more nearly approaching 0.05 mm. By repeating this process a few times this intermediate portion will be reduced to particles whose diameters are very near 0.05 mm. and which may be divided between sand and silt, according to judgment. The amount of this is usually very small. As soon as portions are separated which the microscope shows to be pure sand or pure silt, they are added to the chief portions of these grades already obtained.

"The same process is applied to the separation of silt from dust. When all the silt has been removed from the dust and clay, the turbid water containing the dust and clay is set aside and allowed to settle in a cylindrical vessel for 24 hours. The vessel is filled to a height of 20 cm. According to Hilgard, the separation of the dust from the clay during a subsidence of 24 hours will give results of sufficient accuracy, although the clay then suspended will not be entirely free from measurable fine particles up to .001 or .002 mm. diameter.

"Small beakers and small quantities of distilled water are used at first for the decantations, as thus the duration of subsidence is less and more decantations can be made in a given time. Beakers of about 100 cc. capacity are convenient for the coarser grades, but it is necessary to use larger vesels for the fine sediments from which turbid water accumulates that cannot be thrown away, as may done with the clear water, from which the coarse sediments settle out in a short time. The water should be kept as small in amount as possible.

"Pestling with a soft rubber pestle and boiling will help to break up the fine lumps of clay.

"A mechanical analysis is made in about 5 or 6 hours, exclusive of the time necessary for collecting the dust and separating the clay, for which a subsidence of 24 hours is allowed.

"The sediments are prepared for weighing by allowing them to subside completely, decanting the clear water as far as possible, rinsing them into a weighed platinum dish, evaporating and igniting. The dish is cooled in a dessicator."

Although soil analysis for agricultural purposes requires great exactness as to the percentages of very fine material, for the purpose of the cement industry this very elaborate differentiation is not necessary. The cement chemist requires to know only how much of a clay is mechanically fine enough for the chemical reaction involved. Generally speaking, we might say that everything passing the 150 mesh sieve (150 mesh to

the linear inch) is sufficiently fine for chemical reaction. But we must not lose sight of the fact that, though reaction by virtue of a higher heat or more lime might be made to take place with particles close to 150 mesh size, after all the most important role is played by much finer grains which cannot be differentiated by mere sieving. The real cement producing magma of Portland cement is formed from the very finest particles of the clay which on vitrification draw the coarser grains into combination. When the potter melts his fritt for a glaze in a crucible, the fine and more fusible portions melt first and gradually bring the coarser and more refractory material into fusion. It becomes important, therefore, to select clays which contain the greatest amount of fine grained matter.

The Ohio Geological Survey has undertaken to study this matter from the practical standpoint. Potter's flint, or finely ground quartzite, was first made the subject of an examination. When mixed with calcium carbonate and heated to 1100°C, it showed on treatment with hydrochloric acid and sodium carbonate solutions, a residue of 28.83 per cent., 71.17 per cent. having gone into solution.

The first thing to do was the carrying out of the sieve analysis, but owing to the fact that sieves differ widely in mesh it was thought necessary to make measurements of the mesh of the different sieves, which are given in the following table:

No. of Sieve.	40	80	100	120	150	200
Space between wires, in inches.....	0.0087	0.0074	0.0060	0.0051	0.0038	0.0031
Remarks.....	Slightly irregular	Regular	Regular	Somewhat irregular	Regular	Regular

The spaces given are the averages of 50 micrometer readings. In the sieve analysis of the flint the following results were obtained:

	Per cents.
Left on 120 mesh sieve.....	1.40
Left on 150 mesh sieve.....	2.36
Left on 200 mesh sieve.....	1.06

In considering the results of a sieve analysis it must be remembered that the particles passing through the sieve are not necessarily round or symmetrical in shape, but may often be needle-like in form, and though they pass through the sieves they are apt to be larger in bulk than particles retained which approach the more ideal spherical shape.

The portion of the flint washed through the 200 mesh sieve was transferred to a 250 cc. beaker and enough water added to make 200 cc. of liquid. The water was now stirred and allowed to settle for one minute

and the supernatant liquid was syphoned off carefully. This operation was repeated till the washings were clear. The residue in the beaker was removed, dried and weighed. Then the washings that had been removed were boiled down to 200 cc., stirred as before and allowed to settle for three minutes and syphoned off. This was continued until finally after three minutes the supernatant liquid was clear. The residue was dried and weighed as before. The third washing was collected, stirred, allowed to settle for nine minutes, syphoned and washed as before. The same operation was repeated for 27 and 81 minutes' settling.

The syphon, with rack and pinion for adjusting its level above the bottom of the beaker, and glass stop cock for controlling the rate of flow together with the sieves, microscope, etc., used in this method of analysis are shown in Fig. 12.

The sediments in each case were carefully examined under the microscope and measurements made of the grains. In the table marked A on page 153 the measurements of particles found in two samples of flint are given. The average dimensions represent 45 measurements.

Since in cement clays the question of the fineness of the quartz grains is the most important question, and since practically everything else offers no difficulty to the chemical combination, this table should prove of some assistance to the cement chemist in making use of the suspension method of mechanical analysis.

The flint samples mentioned, when analyzed mechanically as given in the method above, showed the average results given in Table B, page 153.

This mechanical analysis represents probably the greatest fineness practiced in commercial dry grinding for the clay industries at the present time.

The fact remains, however, that the cement chemist has but little time at his disposal in the daily rush of his routine work, and the mechanical analysis, if made at all, must be carried out rapidly. It is possible to obtain results sufficiently valuable by making only one sedimentation, with one minute settling, obtaining the amount of all particles finer than this sediment, 0.0021 inch, by difference.

Thus the process might be carried out as follows: Weigh out 5 grams of the sample, make up into a thin slurry and wash cleanly through the 40, 100, 150 and 200 mesh sieves The washings from the last sieve are caught in a 250 cc. tall, narrow beaker, stirred, allowed to settle for one minute and the supernatant liquid syphoned off. Fresh distilled water is now added to the sediment in the beaker, thoroughly stirred, allowed to settle for one minute and syphoned off as before. This is repeated till the water added to the sediment no longer is turbid. After the last decantation the residue is transferred to a weighed porcelain or metal dish and weighed. The sum of the weight of the residues on the four sieves

plus the weight of the sediment subtracted from 5 grams will give the weight of all the particles finer than the one-minute sediment. The addition of a drop or two of ammonia or boiling the water will usually deflocculate any aggregate of clay particles. This mechanical analysis works especially satisfactorily with limestone, clay and raw cement mixtures and it is possible to carry out this analysis in one hour.

Fig. 13. Syphon and apparatus for analysis by sedimentation.

Mechanical Analysis of Ground Cement.--The same process may be carried out with ground cement, but in place of water some liquid not acting upon the cement must be used. Alcohol redistilled over caustic lime was

Table A.—Showing Dimensions of Grains of Flint Obtained in Different Sedimentation Periods.

	Maximum dimensions found, in inches.		Minimum dimensions found, in inches.		Average diameter (average of 45 measurements) in inches.	
	No. 1.	No. 2.	No. 1.	No. 2.	No. 1.	No. 2.
1 minute settling	0.008	0.0088	0.0008	0.0004	0.00212	0.00210
3 minutes settling	0.0032	0.0016	0.0004	0.0002	0.00086	0.00088
9 minutes settling	0.00096	0.00110	0.00014	0.00014	0.00041	0.00044
27 minutes settling	0.00055	0.00055	0.00003	0.00007	0.00026	0.00026
81 minutes settling	0.00055	0.00048	0.00003	0.00003	0.00013	0.00014

Table B.—Mechanical Analyses of Potters' Flint, by Sieves and Sedimentation.

No.	Left on 40 mesh sieve. Per cent.	80 mesh. Per cent.	100 mesh. Per cent.	120 mesh. Per cent.	150 mesh. Per cent.	200 mesh. Per cent.	1 minute settling. Per cent.	3 minutes. Per cent.	9 minutes. Per cent.	27 minutes. Per cent.	81 minutes. Per cent.	240 minutes Per cent.	720 minutes Per cent.	Remainder Per cent.
1	0.02	0.12	0.282	0.71	1.05	1.24	23.94	18.93	8.50	7.44	5.74	1.59	0.22	30.21
2	0.01	0.20	0.48	0.78	2.36	1.06	24.74	17.84	9.30	8.02	7.04	1.63	....	....
Av. diam., inch.	0.0087 †	0.0074 †	0.0060 †	0.0051 †	0.0038 †	0.0031 †	0.0021	0.00086	0.00041	0.00026	0.00013	....	....	....

†From dimensions of space between wires of sieves.

used very satisfactorily. Careful tests by Professor Edward Orton, Jr., of the dissolving action of alcohol upon cement showed that practically nothing was brought into solution.

The specific gravity of the alcohol used fluctuated around 0.811. In determining the sizes of the various sediments a well-known brand of Portland cement was used and the following results were obtained:

Sediment.	Maximum size in inches.	Minimum size in inches.	Average size in inches.
1 minute settling	0.008	0.0002	0.00200
3 minutes settling	0.002	0.0002	0.00072
9 minutes settling	0.00075	0.00007	0.00030
27 minutes settling	0.00034	Too small to measure	0.00020

The average size is obtained from 50 measurements.

Under the head of physical testing of Portland cement attention will be called to the importance of the mechanical analysis of cement.

Analysis by the Elutriation Method.—This fine method depends on the fact that the carrying power of a current of any liquid is a function of the velocity. Knowing the velocity of a current of water, for instance, we can determine the size of the particles removed by it, and constructing an apparatus in which a sample of clay or soil is subjected to washing by an upward current of water, by starting with a given low velocity we can remove the fine grains, clay substance and dust completely, so that with this velocity after awhile the flowing water is perfectly clear. If, now, the velocity is increased the larger particles will be carried off, and so on.

The law governing this separation is governed by Newton's law of gravity and is modified as follows:

$$d=v^2\frac{3z}{4g(s-1)}$$

Where d is the diameter of the particle, assuming that all grains are spherical, v the velocity of the water current, g the acceleration of gravity, 9.81 m, s the specific gravity of the particle and z a constant depending upon the surface conditions, its mean value being 2.65. The expression, by substituting the above values, becomes:

$$d=v^2 0.0000255 \text{ millimeters.}$$

This formula assumes that all particles are of equal hydraulic value and that they are spheres of uniform diameter.

The result of many analyses have shown that the above formula must be corrected to

$$d=v^{1.11}\times 0.0314 \text{ millimeters.}$$

in order to correspond to actual conditions. This agrees very well with the results obtained for all velocities between 0.1 mm. and 12 mm. per second, which corresponds to the ordinary clay and silt elutriation.

The apparatus which is used to carry out this method of separation has probably first been used on an extensive scale by Noebel. But considerable improvements have later been made by Dietrich, Masure, Schoene and Mayer. A good method of working and a very satisfactory apparatus have been worked out by Mayer, who improved the Schoene silt apparatus.

But all of these methods, though extremely useful for exact separations, are too elaborate to be used in daily routine of a cement works laboratory, and hence cannot be discussed here in detail. There can be no doubt that the method of moving liquid is more accurate than the subsidence method. For most rigid scientific accuracy the Hilgard method using a perfectly cylindrical funnel and a mechanical stirrer is considered the best. Yet the fact remains that for all around simplicity and rapidity of working the subsidence method must remain the one most satisfactory.

SPECIAL ANALYTICAL AND PHYSICAL PROBLEMS CONNECTED WITH CEMENT ANALYSIS.

Among the problems of indirect importance to the practical cement manufacturer, but of theoretical interest to the chemist, are such problems as the amount of free lime in cement, the amount of chemically combined water in hardened cement, the amount of ferrous and ferric iron present, the condition of the sulphur in the clinker, whether sulphide or sulphate, the degree of absorption of sulphur from the fire gases, the alkalinity of different cements, the melting points of cement and cement mixtures, the effect of the composition and rapidity of cooling upon the crystallization, the heats of solution and hydration and many other problems.

Briefly considering these various problems, we find that the question most profoundly interesting cement technologists has been the query as to the amount of free lime present in cement. This problem has been attacked from all sides, and with practically no results. Thus Liamin, a Russian investigator,* endeavored to determine the amount of free lime by calculations from the amount of water given off at different temperatures. Tomei based his work on the action of ammonium chloride on Portland cement, while Hauenschild used other solutions of ammonium salts. Rebuffat made use of a sugar solution, while Zulkowski used a very dilute acid solution. Steuer allowed hydrogen sulphide to act upon water in which Portland cement had been poured; Wormser and Spanjer made use of an alcoholic solution of aluminium chloride for leaching out the calcium oxide, while Hart employed a 10 per cent. alcoholic iodine solution. Wagner studied the action of carbon dioxide upon cement heated to a red heat, and finally Passow made use of the fact that heat is evolved when calcium oxide combines with carbon dioxide at a red heat.

H. W. Wiley, Agricultural Analysis, p. 218.

Two investigators, Keiser and Forder, endeavored to determine the free lime by estimating the water taken up in the hydration of the cement during the first short interval of the setting, claiming that the calcium oxide is practically all hydrated in a short time, while the calcium silicate requires a much longer time.

The study of the dehydration process of cements has been taken up by a number of investigators like Bauschinger, Rebuffat, Zulkowski, Newberry and the writer, but the result has been far from satisfactory, owing to the physical conditions which interfered with accurate work. However, by using suitable precautions and refinements of operation, there is no reason why accurate and consistent determinations should not be made. The main difficulty so far has been the density of the test pieces, which on the one hand did not permit of complete hydration, and on the other hindered the expulsion of the water of hydration.

The condition of the iron in cements has been one of the points in dispute, but numerous determinations made have shown that the iron is principally in the ferric condition. This investigation is an interesting one and should be more thoroughly worked out for American cements. Three students in the laboratory of the writer in examining three standard American cements burnt in the rotary kiln found likewise most of the iron in the ferric condition.

Of practical as well as theoretical interest is the question of the sulphur in cements, the changes it undergoes in the burning process and the rapidity with which the sulphur of the fire gases is taken up by the basic cement mixture.

Theoretical experiments as to the alkalinity of cements might prove to be of interest and might be carried on along lines similar to the work of W. Richter, who, for instance, found that well burnt properly proportioned cements do not react with phenol phthalein.

On the physical side, much work remains yet to be done. Some important physical constants of the cement constituents are still lacking, such as the determinations of the melting points, the heats of solution and hydration, and the miscroscopic study of the principal minerals in the cement slag has not been carried as far forward as should be done. Since the advent of practical electrical furnaces for high temperatures no insurmountable difficulties stand in the way of such research.

In closing the subject of the chemical and physical examination of Portland cement materials a few words may not be out of place in regard to the status of the American cement chemist. There is a more or less well defined tendency in American cement plants to slight the position of chemist by the paying of insufficient salaries, and hence the places are sometimes filled by men with very little technical training beyond the routine of the analytical work. As a result, we find some brands of cement on the market varying to a degree which is inexcusable and which should seriously impair the reputation of the brand on the

market. The most important position around a cement plant is often filled by a poorly paid man, who is not capable of doing the best work which can be done in his line. The works, however, are in charge of a well paid mechanical engineer, often entirely ignorant of the chemical principles underlying cement manufacture. The chemist is relegated to his laboratory where he has little voice in the management of mill affairs, although on him rests the chief responsibility for the quality of the cement. This state of affairs is partly the fault of the chemist and largely the fault of his college training. The usual academic course in a college, with a little elective work in chemistry, does not fit a man for a responsible industrial position, nor does even a good course in pure chemistry. The training of an industrial chemist should be stronger along engineering lines that it is now, with enough work in chemistry to give him clear conceptions of the entire field of chemistry. This can be done in four years, although five years' training would be much more desirable, in spite of what has been said by prominent teachers in chemistry who seem to think that all the time should be spent in studying pure chemistry. Practical experience has shown the writer that the pedagogical value of the study of chemistry is greatly enhanced if supplemented by the study of engineering subjects in an elaborate course of industrial chemistry. Greater mental accuracy is attained and broader conceptions. The subject of industrial chemistry cannot be properly taught except by men who have had at least several years of practical experience in the industries. The teaching of purely college men will invariably lack force and life in industrial topics. As a rule, the average course in industrial chemistry is more or less of a farce, and does not bring out the main principles of combustion, ignition, drying, crushing, grinding, screening, and separating, filtration, etc., with sufficient clearness. But even though the chemical part of the work is unsatisfactory, if the course as a whole contains sufficient general engineering, it will tend to produce men more valuable to the industry. What the American Portland cement industry chiefly needs is well-trained chemical engineers to take the place of the mechanical engineers who are now trying to manage an industry for which their training has not prepared them.

CHAPTER IV.

MANUFACTURE OF POZZUOLANE AND NATURAL CEMENTS.

POZZUOLANE CEMENTS.

Owing to the comparative unimportance of the true pozzuolane cements, but little attention can be given this subject. The preparation of pozzuolane cement is extremely simple and may be carried out in two ways:

1st. Grinding of pozzuolane rock together with dry calcium hydrate.

2nd. Grinding of pozzuolane alone and mixing it with slaked lime in the wet when used.

Cement made in the first way is, of course, ready for use, and in building need only be mixed with water and sand to be available as mortar. The lime used should be thoroughly slaked and must be dry. When prepared by the second process, care must also be taken to use thoroughly slaked lime. In Europe the second practice prevails, although some authorities urge the preparation of pozzuolane mortar on a large manufacturing scale by the first method. R. Feret advocates the grinding of pozzuolanes as producing a more uniform and satisfactory material. In some places, as in the construction of the Kaiser Wilhelm ship canal, the pozzuolane, which was trass, was ground together with the lime at the works under construction.

Tetmayer has done considerable work with natural pozzuolanes and from his many results the following figures are quoted:

Trass No.	Proportions by Weight.			Tensile strength in pounds per square inch.			
	Trass.	Lime.	Sand.	28 days.	84 days.	1 year.	2 years.
1...	0.66	0.33	3.00	142.8	240.8	249.2	253.4
	0.66	0.33	1.00	158.2	317.8	280.0	291.2
2...	0.66	0.33	3.00	239.4	343.0	309.4	316.4
	0.66	0.33	1.00	187.6	264.6	319.2	351.4
3...	0.66	0.33	3.00	65.8	124.6	207.2	240.8
	0.66	0.33	1.00	81.2	170.8	161.8	320.6

As has already been indicated, the importance of natural pozzuolanes consists principally in the fact that when added to Portland cement they improve the resisting quality of the latter, especially against the action of sea water; but pozzuolane mortar alone, owing to its porosity, is poorly suited for sea water work, and could not be used with any degree of success. The experiments in regard to the benefit of pozzuolane additions are, however, by no means completed.

In some districts along the Rhine and in many localities in Italy the pozzuolanes are simply screened and made up with lime like ordinary sand, this method being quite satisfactory for ordinary work. In the building of Austrian railways the proportion of 1 part lime to 3 parts pozzuolane was found to be the best.

SLAG CEMENT.

General Considerations. —When fused basic blast furnace slag of the composition already indicated in the chapter on "Raw Materials" is suddenly quenched in water, the rate of cooling is, of course, the most rapid possible. If, as is generally assumed, slow cooling is associated with the breaking down or dissociation of complex mineral compounds into simpler ones it is evident that the quenched slag is not given a chance to do this. It must, of necessity, remain the complex glass it was when in fusion. This granulated slag on being mixed with lime produces, as we know, a hydraulic cement of considerable strength. Yet the same slag cooled slowly shows but little hydraulic strength. We are evidently in this instance dealing with a far-reaching molecular change.

Work of Zulkowski.—The first to realize that he was dealing here with isomeric compounds and to scientifically investigate these was Professor Zulkowski, of the University of Prague.* Though his work has been considerably criticised, it must be acknowledged that it brings out fundamental principles which cannot be ignored. They bear important relations to the general question of hydraulicity whether referring to slag or to Portland cement.

Glass, an amorphous mixture of silicates, or a solution, as we may call it, when heated for some time at a low temperature, will be found to crystallize, as we can observe when the glass combustion-tube used in chemical work assumes a porcelain-like appearance after long use. On examination these crystals have been found to be the simple monocalcium silicate, wollastonite. All slags, whether basic or acid, may likewise be called glasses with the same tendency to crystallize on slow cooling. In recent experiments** definite minerals have been recognized as uniformly appearing in all basic slags, some of them predominating in strongly hydraulic and others in feebly hydraulic slag. And it is of

*Die Chemische Industrie, 1889, p. 60.

**Dr. Passow, Stahl und Eisen, Aug. 1st, 1903.

special interest to note that some of these minerals are identical with those found in Portland cement. Five of these minerals have been found. The principal ones are:

1st. A white crystalline mineral, high in lime, called alite, found in rapidly cooled basic hydraulic slags, and all Portland cements.

2nd. A double refracting mineral showing distinct parallel striations found in all slags and cements of inferior hydraulic value and showing a tendency to fall to a powder. This is called felite.

3rd. A glassy, usually dark-colored mass of good hydraulic value, in fact being equal to the alite in cementing quality. Of course, only the glass-like mass appearing in basic slags, and Portland cements, is meant here. The glassy constituent which predominates in acid slags has no hydraulic properties. Quenched basic slags show this glassy component in predominating quantity.

Zulkowski assumed that the hydraulic mineral varieties of basic slags are preserved only by rapid cooling, while on slow cooling they break down to simpler non-hydraulic compounds. This agrees very well with practical results, inasmuch as we know that frequently Portland cement mixtures produce excellent cements when burnt rapidly, but "dust" or form a slightly hydraulic powder when burnt slowly. This cement producing constituent, whether found in slags or Portland cements, Zulkowski called "hydrolite," which as we now know consists essentially of alite or cement glass, or both.

By treatment with dilute acid Zulkowski endeavored to separate the constituents of the slowly and rapidly cooled slags which, of course, is a crude and unsatisfactory procedure, and his earlier results based on this work deserve little attention. But he brought out the very interesting fact that quenched basic slag, though possessing cement qualities, brings out its inherent maximum hydraulic value only when mixed with a small percentage of slaked lime. Zulkowski now looked into this question by treating granulated slag not only with lime, but also with strontium, barium, and alkalies. All of these showed the same behavior, and caused the slag to become a good cement. It was also found that the compound thus added did not combine chemically with the slag itself. Thus, for instance, the alkalies could be washed out from the hardened cement after they had caused the slag to harden. Water alone evidently is the reacting substance in uniting with the hydrolite to form a hydrous silicate. Caustic lime simply accelerates and assists this absorption. Very basic slags do not need an addition of lime. Having arrived at this conclusion, Zulkowski at once was able to trace the analogy between slag and Portland cement by saying that the latter consists of the same hydrolite as the slag cement plus free lime. Portland cement, therefore, like very basic slag, does not need an addition of lime.

On experimenting with the slag, which alone hardens slowly in water, it was found by means of the microscope that it consisted of small glitter-

ing grains like pulverized glass. On adding water to 20 grams of the ground slag, the sandy portion settled first and then a heavy flocculent mass was precipitated. At the same time the volume of the powder constantly increased until it was about twice the original volume. The appearance of this hardened powder did not differ essentially from that of the dry slag. But this action is much more energetic if alkalies, barium, or lime water is added. The volume becomes three to five times the original volume, and assumes the colloid character. The mass hardens very rapidly, and the small grains of slag change to swollen, rounded particles.

The conclusions of Zulkowski may be summarized as follows:

1. The blast furnace slags, suitable for the manufacture of cement, are highly basic meta-silicates whose decomposition is prevented by rapid cooling or granulation.

2. Owing to their anhydrous condition, they have a tendency to unite with water and to harden, which is assisted by the presence of alkalies. Such silicates may be called hydrolites.

3. On slow cooling, an inter-molecular decomposition of the meta-silicate or hydrolite takes place in a greater or smaller measure. During this process the mass loses its uniformity, and the constituents are not dissolved by weak acetic acid in the proportion in which they are present in the slag.

4. The hydration of the powdered basic meta-silicate is coincident with a change in volume, and a change in the shape of the grains, which now fill all the space, and gradually harden to a compact mass.

5. Slags cooled slowly, which contain only certain components or isomeric compounds of the above meta-silicates, do not possess the properties of the hydrolite, mentioned under 2 and 4.

6. Portland cement, like slag cement, is a mixture of a hydrolite analogous to granulated furnace slag, and as much lime as remained uncombined on burning. The difference between the two is only that the necessary lime must be added to the slag in the shape of calcium hydrate.

7. The calcium oxide of Portland cannot be separated directly.

8. The calcium oxide may, however, be removed from Portland cement by a special treatment with dilute hydrochloric acid in greater or smaller amounts, and the hydraulic property is diminished accordingly. The residue remaining behaves like highly basic slag; that is, it hardens in the presence of the alkaline compounds without combining with them chemically.

9. But since the calcium oxide is thus removed in the wet way, the cement is sufficiently hydrated and the residual cement can never attain its original strength. The hydraulic agent of Zulkowski is represented by the structural formula, Fig. 14, which hydrates to Fig. 15.

This formula is thus seen to be deduced from a basic meta-silicate which hydrates by the taking up of a molecule of water.

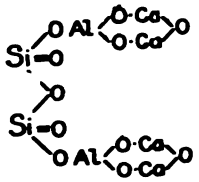

Fig. 14. Zulkowski's formula for hydrolite, before hydration.

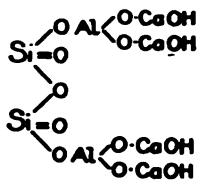

Fig. 15. The same after hydration.

Chatelier arrives at different conclusions by assuming that the granulated slags combined with lime are rendered chemically active by retaining the latent heat otherwise given off in crystallization. Prost has investigated this point and has really found that crystalline (slowly cooled) slag on dissolving in hydrochloric acid evolved 301 calories, while the granulated slag gave off 420 calories.

Selection and Granulation of Slags.—The limits of composition have already been given by the values established by Tetmayer, and it might be said that the more basic the slag, the better suited it is for cement making. The slags especially suitable for this purpose show from 27 to 32 per cent. silica, 10 to 22 per cent. alumina, 48 to 56 per cent. lime, 1 to 2 per cent. magnesia. The sulphur content should be carefully watched and never allowed to run above 1.25 per cent.

It is of the greatest importance to reject any slag not suitable for cement making and to make use of it in connection with the manufacture of slag brick, for which purpose the slag may be of inferior quality, that is, much less basic. In this manner it is possible to maintain a higher grade of excellence without financial loss. It is advisable therefore to have a slag brick outfit in connection with a slag cement plant. The fitness of a slag is determined by chemical analysis, which must be supplemented by physical tests; the dried granulated slag must be ground together with varying proportions of dry slaked lime, usually from 5 to 15 per cent., and tested for tensile strength and constancy of volume as prescribed by the standard cement specifications.

The granulation may be carried out in two ways: by means of a stream of water or by means of a blast of air. There is no question but that the first method is the more satisfactory one, resulting in the best quality of granulated slag, but it has the disadvantage of producing a wet slag which must be dried. The amount of water retained by the slag is not great, however, and hence the extra cost of manufacture is not an important factor. Some theoretical advantages, on the other hand, are claimed for the air cooled slag, but these are not proved sufficiently by actual results. The slag is granulated by means of a flat

stream of water about 6 inches wide under as great a pressure as possible. In one case known to the writer the water is under a pressure corresponding to a 70 foot water column. The effect upon the molecular structure of a slag by granulating it by means of water has already been discussed. Practically the effect is extremely marked. A French engineer, H. Detienne, has approached the point from the practical standpoint, by grinding granulated and ungranulated slag together with equal amounts of hydrated lime. The cements thus produced were made up with standard sand in the proportion of 1 part of cement to 3 parts of sand, and tested for tensile strength. After 28 days the ungranulated mixture showed a tensile strength of 60.2 pounds per square inch, while the granulated slag mortar indicated 126 pounds. Tetmayer found much greater differences owing probably to the fact that Detienne used samples of slag cooled rapidly in the air and also did not grind his cement very fine.

The water used in granulation probably does not enter into combination with the slag to any extent, and the only change is the removal of part of the sulphur of the slag, going off as hydrogen and calcium sulphides. Granulation of the semi-solidified slag has but little effect on its hydraulic value.

Drying.—The granulated slag, after its excess of water has been allowed to drain off, is conveyed to the dryer; a rotary dryer 30 feet long and 5 feet in diameter, fired either with gas, crude oil, or coal is the most satisfactory. It has often been asked how slags too high in sulphur might be improved by the complete or partial elimination of this injurious ingredient, and it has been proposed to carry on this refining process during the drying operation. But as yet no definite or satisfactory scheme has been worked out. The use of steam and carbon dioxide has been suggested and some work has been done along this line. It seems that the use of steam offers a promising process, since it has been shown that the calcium sulphide is to a large extent decomposed by it. If, however, saturated steam is to be used, it is evident that this treatment must precede the drying owing to the condensation of steam. If, on the other hand, superheated steam is used, which also is the more efficient, the two processes could be combined. The dryer would have to be made much longer in this case, as long as a rotary kiln, 60 feet. By introducing the steam at a distance of, say, 20 feet from the discharge end of the apparatus and the hot gases from the coal fire, gas jet, or oil burner at the lower end as usual, condensation at the discharge end would be avoided entirely. The temperature of the steam should not fall below 300° C. In this connection it might be stated that the sulphur present as calcium sulphate evidently can not be expelled by this procedure. By maintaining reducing conditions of the fire gases, the expulsion of sulphur should be assisted most decidedly, especially if the temperature ap-

proaches red heat. However, the whole scheme, as has been said before, needs to be tested on a large scale before it can be pronounced commercially feasible.

Intermediate Grinding.—From the dryer the slag is conveyed to iron cooling bins, and then to the intermediate grinding machinery, that is, machines which grind sufficiently fine so that the bulk of the material passes the 20 mesh sieve. These machines may be ball-mills, disintegrators, Kent mills, rolls, dry-pans or buhr mills. We cannot discuss the relative merits of these machines here, since it will be necessary to study them more in detail in the chapter devoted to Portland cement, but it may be said that the machines more commonly employed are the ball-mill, the disintegrator and the Kent mill. Each of these machines will do the work satisfactorily. Although they may differ in efficiency, these differences are not very pronounced with material like granulated slag.

The roll crusher, as far as cheapness of operation is concerned, is more efficient than any of the three preceding machines, but, probably owing to its aptness to choke when overcrowded, the unequal wear and the small amount of fine material it turns out, it has not found as general application as this system really deserves.

The drypan, although a machine of great capacity, occupies much room and does not do as uniform grinding.

As to the buhr mill, it must be classified as a wasteful machine, in regard to power consumption, besides requiring constant attention owing to the dressing of the stones. A higher claim of efficiency can be made for the emery mills in which the latter item is reduced considerably.

The Lime.—After leaving the intermediate grinding machine, the slag is taken to a bin in order to be delivered to the fine grinding machines. At this stage the hydrated lime is added.

The amount of lime to be added varies, and must be determined for each individual slag, by grinding the dried granulated slag together with varying amounts of dry, slaked lime, and applying the various cement tests. In the majority of cases the addition of lime necessary will fluctuate between 5 and 15 per cent., being usually closer to 5 than to 15 per cent. The lime is ordinarily bought as quicklime, and is slaked at the cement works, though of course a considerable saving might be effected by burning it at the plant, since limestone is invariably shipped to blast furnaces to be used as flux, and never comes a great distance. As to the burning, it could be accomplished in an ordinary limekiln, operated continuously, using coal or blast furnace gas as fuel. The lime should be as low in clay and free silica as possible in order that it may slake freely and not give rise to hard lumps which slake slowly and give trouble when ground with cement. Such slowly slaking lime, though finely ground, will invariably cause difficulties owing to its increase in volume when the

cement itself has set to a hard mass, giving rise, of course, to cracking or swelling.

Methods of Preparation of the Lime.—Although slaked lime can now be purchased on the market, it will usually be found too expensive. Slaking may be carried on: first, by the old pile slaking; second, by the periodic cylinder method; third, by the continuous slaking machine. In the ordinary pile slaking a heap of quicklime is made, as much water sprinkled over it as practice has shown to be necessary, and allowed to slake for some time. The slaked lime is then put through a 10 mesh screen, which may either be a long stationary inclined screen or a mechanically driven rotary sieve. It is obvious that too much water will have the effect of producing a moist hydrate which cannot be screened, and hence the addition of water must be carefully gaged. The screened lime is now taken to a cast iron pan, about 15 feet long, 8 feet wide, and 12 inches deep, kept heated by means of a furnace beneath. When dry, the slaked lime is scraped from the pan and put through a 20 mesh screen. By means of a conveyor, the hydrated lime is taken to the bin ready to be used.

In the cylinder method of slaking a large quantity of quicklime, say one ton, is dumped into a steel cylinder provided with a large manhole and swung on trunnions. The manhole is then closed and through a pipe the requisite amount of water is introduced. The heat given off by the hydration soon converts the excess of water into steam under a great pressure. A safety valve must be provided to relieve any excessive pressure. Slaking thus takes place under pressure, and the slaked lime is in the condition of a powder. It has also been proposed to revolve the cylinder in order to accelerate the slaking. After the slaking is completed, the cylinder is placed in position with manhole down and the lime dumped into suitable receptacles.

In the third method, which has so far not been worked out on a practical scale to the writer's knowledge, but which has the great advantage of continuous operation, three stages are to be noted. The first part of the process, the slaking, is carried on in long, tubelike cylinders, about twelve feet in length, somewhat similar to a clay pugmill, in which two shafts provided with blades revolve rapidly. At the feed end where the quicklime is brought in as powder, water is sprayed in under pressure, somewhat in excess of the amount required, which must be, of course, gaged by an attendant. The rapidly revolving knives or blades bring about through blending of the lime with water. At the discharge end of the machine, the hydrated lime is taken to a large sheet iron bin, of such dimensions that the lime is allowed to remain in it for two or three hours. At the bottom of this bin a revolving feeder is arranged which feeds the slaked lime into a rotary dryer in which the material is dried by a current

of hot air, produced by passing the air through an iron coil heated by a furnace. The dried lime is then run through a disintegrator and again converted into powder. This method, being continuous, evidently must result in a much greater capacity than could be attained by either of the other methods.

The Addition of the Lime.—The lime hydrate, whatever may be its preparation, is added to the granulated slag coming from the intermediate grinding machine and now stored in a bin above the fine grinder. The mixture may be accomplished by a mechanical feeder, consisting of an iron disc revolving beneath both the slag and the lime bin, so that both materials are fed upon it, the slag through an aperture whose area is to the area of the lime feed hole as the proportion of slag is to that of the lime necesary. It is evident, of course, that both of the apertures must be adjustable. As the disc revolves, a scraper turns off the two materials into the screw conveyor, feeding the fine grinding machines. Another device observed at an Ohio slag cement plant was a flat slider similar to an engine slide valve having a reciprocating motion and moving beneath the slag and the lime bin. It had two sets of holes, large ones for the slag, and smaller ones for the lime. With each stroke of the slide, a quantity of slag and lime was allowed to fall through these holes for a short interval of time. In some plants the slag and lime are weighed out by means of scale cars and dumped into a small bin feeding the fine grinders.

Fine Grinding.—As fine grinders, there are two machines to be considered principally; the tube mill and the Griffin mill. The former is a machine resembling a tube, from 18 to 22 feet in length and about 5 feet in diameter, into which the slag is fed and from which it is discharged continually. The grinding is done by means of flint pebbles filling the machine to slightly above the axis. Beside the grinding action proper, this machine affords a splendid blending of materials approaching almost ideal mixing. At the same time it eliminates the use of all screens, the required fineness being obtained by the rate of feeding. On the other hand it consumes much power.

The Griffin mill might be compared with a mortar and pestle, since it consists of a revolving conical pestle weighing about 100 pounds, and about 18 inches in circumference, suspended from a universal bearing. When in motion the pestle is pressed against a steel ring by centrifugal force and thus effects the grinding. This ring is about 6 inches high and a little over 30 inches in diameter. The pestle itself revolves about its own axis, thus rolling against the surface of the ring. By means of fan blades, above and below the cone the fine particles produced are blown through screens surrounding the grinding space.

There are several other mills on the market similar in principle to the Griffin mill, like the Huntington mill, the double pendulum mill using two rolls in place of the one of the Griffin mill, and others.

As far as the grinding proper is concerned the efficiency of these mills is undoubtedly higher than that of the tube mill, but owing to the factor of centrifugal force they do not accomplish the thorough blending of the former. In fact since the expression for the centrifugal force

$$C=\frac{Wv^2}{g\ R}$$

involves the factor of the mass of the particles it is readily seen that there must be a tendency to segregation of unlike particles of different sizes and weights. In the manufacture of slag cement we blend two materials, slag and calcium hydrate, having the specific gravities 2.8 and 2.1 respectively, and it seems quite evident that the blending accomplished by the Griffin mill is bound to be inferior in quality as compared with the work of the tube mill.

From the fine grinding machine the ground slag cement is conveyed to the storage bins and is ready for shipment, since it is not necessary to "cure" slag cement as is the case with Portland cement.

Testing of Slag Cements. —In first bringing out a slag cement, it is of great importance to subject it to the most rigid tests known to the manufacturer in order to determine, as far as it is possible to do so, its properties and ultimate behavior in use. The tests employed are the same to which Portland cements are subjected, special attention being paid, however, to the tests for constancy in volume. Finely ground slag cement of the proper composition, containing not more than 1.3 per cent. of sulphur and 3 per cent. of magnesia will, as a rule, produce a sound cement. A peculiar color phenomenon is noticed in the hardening of slag cements in water, the change of the first bluish gray color to a pronounced green color, which, however, disappears in time. This is probably due to the reaction:

$$CaS+H_2O+FeO=FeS+Ca(OH)_2.$$

The sulphide gradually changes to calcium sulphate which, owing to its solubility, is brought to surface by water and appears as a white efflorescence. The remaining calcium sulphide also oxidizes to calcium sulphate, forming crystals in the interior. This salt plays an important function as regards the durability of the cement, since on oxidation it suffers a decided increase in volume which tends to break up the hard mass of the cement. In water this effect of crystallization is less apparent, and hence all slag cements, especially those high in sulphur, are at a disadvantage when hardening in air or exposed to it after hardening, and show their best strength only in work under water, foundations, etc. They are unsuited for work exposed entirely to the air like in sidewalks.

Another disadvantage is the tendency to effloresce, made mention of above. On the other hand it has been claimed that in sea water construction and all other subaqueous work, slag cement appears exceedingly well; in fact, some claim for it superiority over Portland cement. Altogether, the slag cement is a hydraulic mortar par excellence. But it cannot be denied that its weak side is the tendency to shrink during the setting stage, so that it must be protected carefully against too rapid drying, and must have plenty of water in order to bring about the complete formation of the colloid hydrous silicates which are the cementing agent. This tendency to shrink or crack is proportional to the content of calcium hydrate, hence it is plain that the content of the latter must be kept as low as possible.

Tetmayer found on preparing cements from mixtures consisting of 100 parts of slag and 20 parts of slaked lime, 100 slag and 40 lime, 100 slag and 60 lime, 100 slag and 80 lime, and making them up into cubes of 7 cm. face, that after 28 days the linear shrinkages were in the above order: 0.034, 0.060, 0.085, and 0.132 mm.

If slag cement fails in the cold and hot tests for constancy of volume, this is almost invariably due to the imperfect grinding of the lime, or the slow slaking character of the latter, or poor slaking or excess of sulphur.

Slag Cement in Ohio.—So for the only plants in Ohio producing slag cement are the Brier Hill Coal & Iron Company, Youngstown, and the Strouthers Furnace Co., Strouthers, but there is no reason why the manufacture could not be carried on by other blast furnaces of the State.

A test of the Youngstown material gave the following results:

	Per Cents.
Silica	28.20
Alumina and iron	11.60
Lime	52.80
Magnesia	2.37
Volatile matter	2.75
Sulphur	1.57
Total	99.29

It left approximately 3.8 per cent. on a 200 mesh sieve. The initial set was 1 hour and 20 minutes; the final set 3 hours and 10 minutes. It stood both the hot and cold test. The tensile strength was as given in table on top of page 169.

Hatt's Results. —Wm. Kendrick Hatt* made extensive examinations of American slag cements which are summarized in second table on page 169.

Engineering Record, Vol. 43, No. 9.

Tensile Strength in Pounds Per Square Inch.

Age.	Neat.	1 Cement : 3 Sand.
24 hours	330	75
7 days	502	223
14 "	610	310
21 "	545	322
28 "	715	348
3 months	655	340
6 "	728	340
1 year	758	343
2 years	768	408

Table of Chemical Analyses of Slag Cements Examined.

Cement.	A	B	C	D	E
Lime.....	55.85	63.50	56.55	54.75	53.30
Silica.....	28.81	19.46	27.48	29.50	20.08
Alumina and iron oxide.	10.74	10.94	10.86	11.02	10.80
Magnesia.....	1.28	2.08	1.75	1.44	3.44
Sulphur as Sulphide....	0.35	.....	0.43	0.30	0.47
Sulphur as Sulphate....	trace	0.35	trace	trace	1.36
Loss on ignition.....	2.31	1.22	3.41	2.73	2.63

Cement E is really not a slag cement, but is made from slag, like Portland cement.

Average of the Tensile Strengths Obtained by Breaking Six Briquettes of Each of the Preceding Five Cements. Pounds Per Square Inch.

Age.	Neat.	1 : 1	1 : 3
24 hours	193	144	39
7 days	404	390	163
28 days	477	403	174
60 days	519	498	208
90 days	507	483	217

A - SLAG CEMENT & SLAG BRICK PLANT

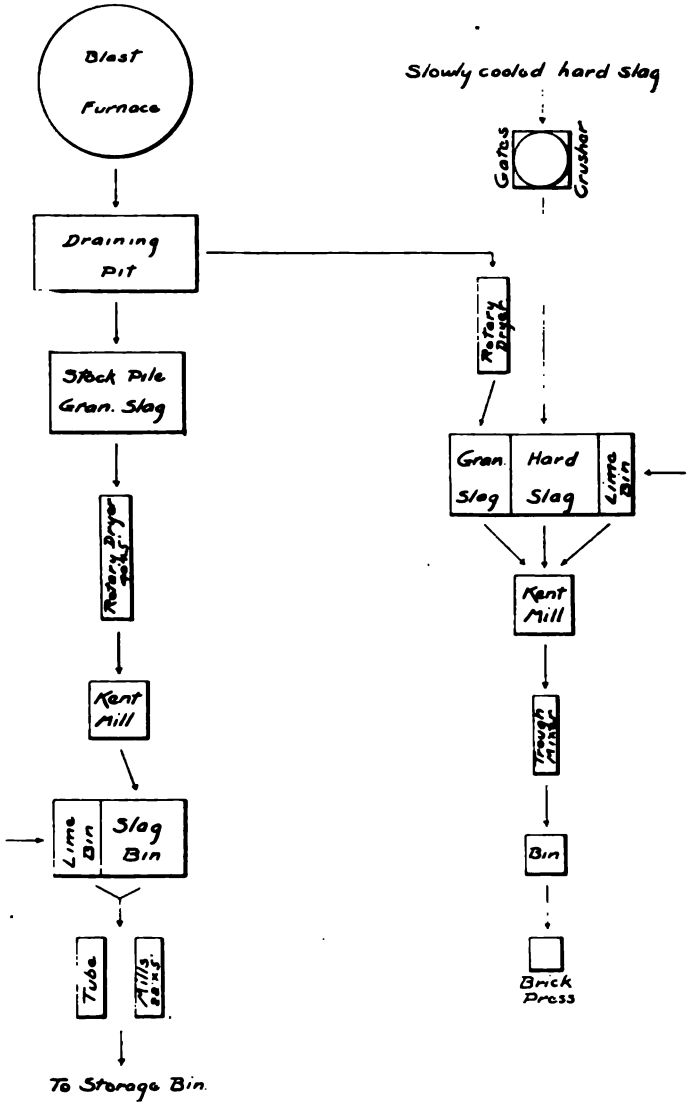

Fig. 16. Ground plan of a plant for manufacture of slag cement, the unsuitable slag being converted into slag brick.

finally pressing the material into bricks by means of a press similar to the dry presses used in clay brick making. The capacity of the largest machine of this kind is about 20,000 bricks per day. In selecting a press for this work care should be taken to see that its plungers are provided with carefully adjusted powerful springs in order that, in pressing, the plungers will give some whenever an excess of material happens to be fed by the charger, thus preventing breaking of the machine. It is hardly necessary to say that the press should be of the heaviest possible construction. In Europe a press is used in which the pressure is applied by a heavy plunger falling freely upon the material in the mold, thus doing away with all possible danger of breakage due to an excessive charge. However, the bricks thus made are not as dense as they should be, and are apt to be crumbly. It is important that the top and bottom dies do not fit too tightly in order to allow the enclosed air to escape. The slag brick should not be taken into a dry atmosphere at once, but should be allowed to remain in a moist room for several days. After two weeks they are, as a rule, ready for the market. It is obvious that in making these bricks Portland cement may be added in smaller percentages and may be used as a substitute for the lime.

MANUFACTURE OF NATURAL CEMENT.

This branch of the cement industry is the simplest one and consists solely in taking the rock as it comes from the quarry or mine, in lumps, burning it in plain upright kilns, and grinding the burnt, friable pieces to a powder. No attempt to regulate or control the qualities of the product can be made except by varying the speed of burning, or by using a higher or lower temperature, and hence the burning becomes the most important operation.

The rock is either quarried or mined. In the quarries of the natural cement mills, all modern quarry appliances are used, steam or compressed air drills and power cranes. High explosives are, of course, universally employed.

The treatment of the quarried cement rock differs in different plants. The more progressive mills crush the rock into two or three uniform sizes by means of Blake crushers, while others make no attempt to crush it, but put it into the kiln in the shape in which it comes from the quarry. It is evident that by crushing the rock, greater uniformity of burning must be the result as well as better utilization of the kiln space.

The rock is burnt until most of its carbon dioxide is expelled, and the stone has become very porous, and is quite friable. It is practically unavoidable that some of the stone be underburnt, and some of it overburnt, that is, burnt to a vitrified clinker. It is endeavored to sort out both kinds as much as possible.

The sorted stone is now conveyed by means of cars or barrows to the intermediate crushing machines, usually a machine of the "corn-sheller"

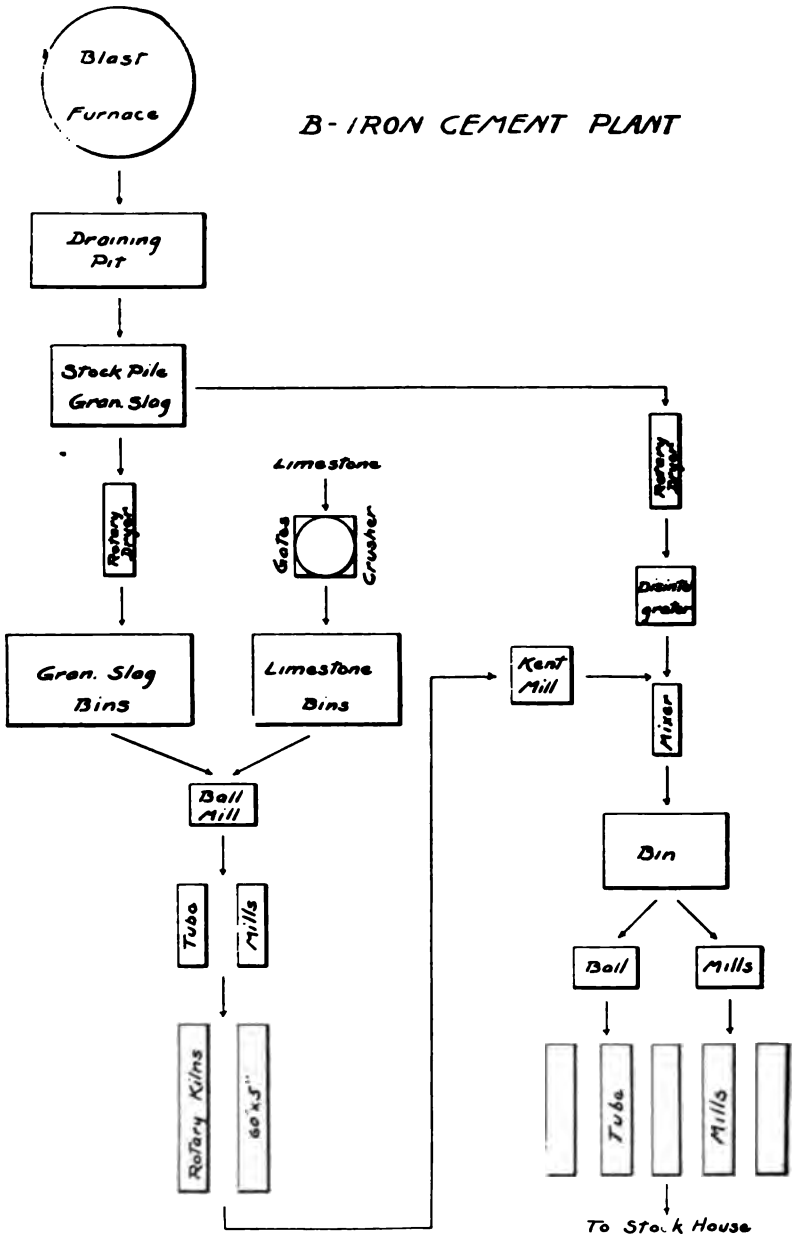

Fig. 17. Ground plan of a plant for the manufacture of "Iron Portland" cement.

type, called a "cracker," which consists essentially of a ribbed, steel-faced or chilled iron cone, revolving within a conical space, the cone being rotated by means of a vertical shaft. From this machine the crushed material is conveyed to screens,which separate the cement which is fine enough to be packed. The coarser particles go on to the fine grinding machines, which in most plants are ordinary mill-stones or emery-faced stones. As a rule the cement is packed at once on coming from the mills.

INVESTIGATIONS ON THE BURNING PROCESS.

We know from the examination of the cement-rock analyses that we must distinguish between calcareous and magnesian rocks, that is, stones high in lime and low in magnesia and those containing more than 5 per cent. of magnesia. The typical Roman cement formula we have found to be: $1.60RO$, $0.23Al_2O_3$, SiO_2.

Mineralogically, we are here dealing with an intimate mixture of carbonates with clay, and mineral detritus of various origin, quartz, hornblende, augite and mica. In burning, the first stage must necessarily be the expulsion of the carbon dioxide; with the production of calcium oxide, the reaction between it and the accessory silicates and silica will begin. It is but natural to suppose that the clay should be attacked first by the calcium oxide, followed by the silicates, and finally by the free silica.

Work of Nauss. —R. W. Nauss investigated this question of the action of calcium oxide on clay and quartz to some extent in his thesis for graduation at the Ohio State University, by making up a mixture of whiting, pure kaolin and quartz (between 120 and 150 mesh) of the following composition in the unburnt condition:

	Per Cents.
Calcium carbonate	70.22
Kaolin	11.05
Quartz	18.66
	99.93

which would correspond in the burnt condition to:

	Per Cents.
Calcium oxide	58.45
Alumina	6.35
Silica	35.30
	100.10

This mixture was made up into briquettes, which were weighed when dry, heated in a kiln to different temperatures, and drawn at intervals above 500° C. The briquettes were then cooled in a dessicator and again weighed. In addition, determinations of the insoluble silica were made by treatment with hydrochloric acid and sodium carbonate solution

and the carbon dioxide was determined approximately by absorption and volumetric measurement. The temperatures were measured by means of the Chatelier pyrometer. In the following table the results obtained by Nauss are compiled.

Reaction of Calcium Oxide upon Kaolin and Quartz.

Number.	Temperature °C.	Loss on burning.	Loss on completed ignition.	Carbon Dioxide remaining	Insoluble silica per cent.	Remark.
1	550	1.79	27.79	28.48	.....	
2	585	1.88	27.96	28.44	.....	
3	610	1.80	28.67	28.84	.....	
4	655	1.91	28.83	27.83	.....	
5	700	4.81	25.17	25.89	.....	
6	725	6.18	24.30	24.58	.....	
7	750	6.99	23.02	23.88	.....	
8	775	8.35	21.90	21.07	19.70	
9	800	12.51	17.94	18.72	.....	
10	850	20.34	10.64	7.32	19.00	
11	900	24.42	5.89	5.29	.....	
12	950	27.56	2.88	2.17	18.90	
13	1,000	30.00	0.60	0.40	18.83	
14	1,050	29.75	.....	.....	18.75	
15	1,100	29.65	.....	.....	18.75	
16	1,150	29.74	.....	.....	18.26	
17	1,150	30.10	.....	.....	16.19	Held at this temperature for 12 hours.
18	1,200	30.10	.....	.....	16.10	
19	1,200	30.10	.....	.....	15.37	
20	1,250	30.10	.....	.....	13.13	Dusted.
21	1,250	30.10	.....	.....	13.34	"
22	1,300	30.10	.....	.....	11.97	"
23	1,300	30.10	.....	.....	10.68	"
24	1,325	30.10	.....	.....	.....	Began to fuse.

The following conclusions may be drawn from Nauss' work:

First. In regard to the decomposition of calcium carbonate, it is clearly shown that it begins to break up between 610° and 650° C., and before 700° is reached the evolution of carbon dioxide is going on quite rapidly. At 1000° the evolution is practically at an end.

Second. On examining the amounts of insoluble residue and comparing the percentage with the known amount of quartz in the mixture, 18.66 per cent., and making allowance for the small amount of quartz in the kaolin itself, it is seen that the kaolin is decomposed completely at 850° C. and almost completely at 800° C.

Third. Free quartz seems to be attacked by the calcium oxide soon after the completion of the decomposition of kaolin, probably at about 950° C., which reaction continues at an increasing rate up to the highest temperature employed in these experiments. It is quite evident, also, that the length of time of burning influences the amount of quartz attacked somewhat, so that by longer burning, at least with temperatures over 1100°, more quartz may be rendered soluble than in a short period of ignition.

A very interesting fact was brought out by the tendency to dust observed with the mixtures burnt at temperatures above 1200°. While at 1200° the briquettes were hard, at 1250°, they dusted very rapidly, and at 1300° almost instantaneously.

On calculating the formula of this mixture from the composition we find it to be $1.77CaO$, $0.108Al_2O_3$, SiO_2, that is, not quite a singulo calcium silicate, and hence might properly be classed within the group of natural cements. It is not difficult to understand that the dusting must be coincident with a significant molecular change from the condition of the loose, friable mixture to a hard body breaking down at once to a powder. Might not this fact indicate that up to 1200° these calcareous mixtures are but pozzuolane-like, simple silicates, consisting of silicate and free base which on further application of heat become chemically more complex and non- or but slightly hydraulic? This view is strengthened by the results of another investigation which has shown that on increasing the free silica, with but sufficient base to convert the quartz into the active state, the hydraulicity is practically as great as with a greater amount of base.

Kennedy's Results.—This subject seems important to the writer, since, evidently, all Portland cement must pass through these reactions, and it is necessary for the proper understanding of the genesis of these cements that we should know something in regard to the initial stages of the formation of the hydrolite.

The expulsion of carbon dioxide from a kaolin-calcium carbonate mixture is pictured rather clearly by the accompanying curve* representing the per cent. of the original weight of briquettes, made up from 70 parts of kaolin and 30 parts of whiting (calcium carbonate) remaining after heating at different temperatures. The time occupied by the experiment was 28 hours. The temperature was increased steadily up to 725°, when this heat was maintained for a little over 12 hours to observe the effect of heat soaking on the briquettes. The temperature was then raised steadily to 1000°. In this curve the interesting fact was brought out that while in pure kaolin the chemical water is expelled between 450° and 600°, the carbon dioxide from the briquettes containing 30 per cent. of the carbonate will prolong the dehydration to 900°. Heat soaking for a comparatively long period is of no advantage, for, though it drives off some additional carbon dioxide, this amount is but small. This agrees with the laws of phase rule.

Investigations Carried on by the Writer.—In order to study further the effect of composition and temperature of burning of the Roman cement type on the resultant hydraulicity the following series was projected and carried out by the writer. Two clay bases were prepared, one consisting of almost pure kaolin and one of a mixture of kaolin and very fine ground quartz, passing a 150 mesh sieve, made up from 56 parts of kaolin, and 44 of quartz. Accordingly, the composition of the two clay bases was:

	Kaolin.	Kaolin quarts mixture.
Silica	46.4	70.0
Alumina	39.7	22.2
Chem. water	13.8	7.7
	99.9	99.9

Starting with each clay base and using a pure grade of commercial calcium carbonate, four mixtures corresponding in composition to the following four formulæ were prepared by grinding wet in a porcelain lined ball-mill:

$$(2.5CaO)SiO_2(CaO)Al_2O_3$$
$$(2.0CaO)SiO_2(CaO)Al_2O_3$$
$$(1.5CaO)SiO_2(CaO)Al_2O_3$$
$$(1.0CaO)SiO_2(CaO)Al_2O_3$$

These eight cements formed one-half of the series, while the other half consisted of mixtures based on the same two clays, but built up with a dolomitic material in place of the calcium carbonate. This dolomite was

* *W. M. Kennedy, Transactions Am. Cer. Society*, Vol. IV.

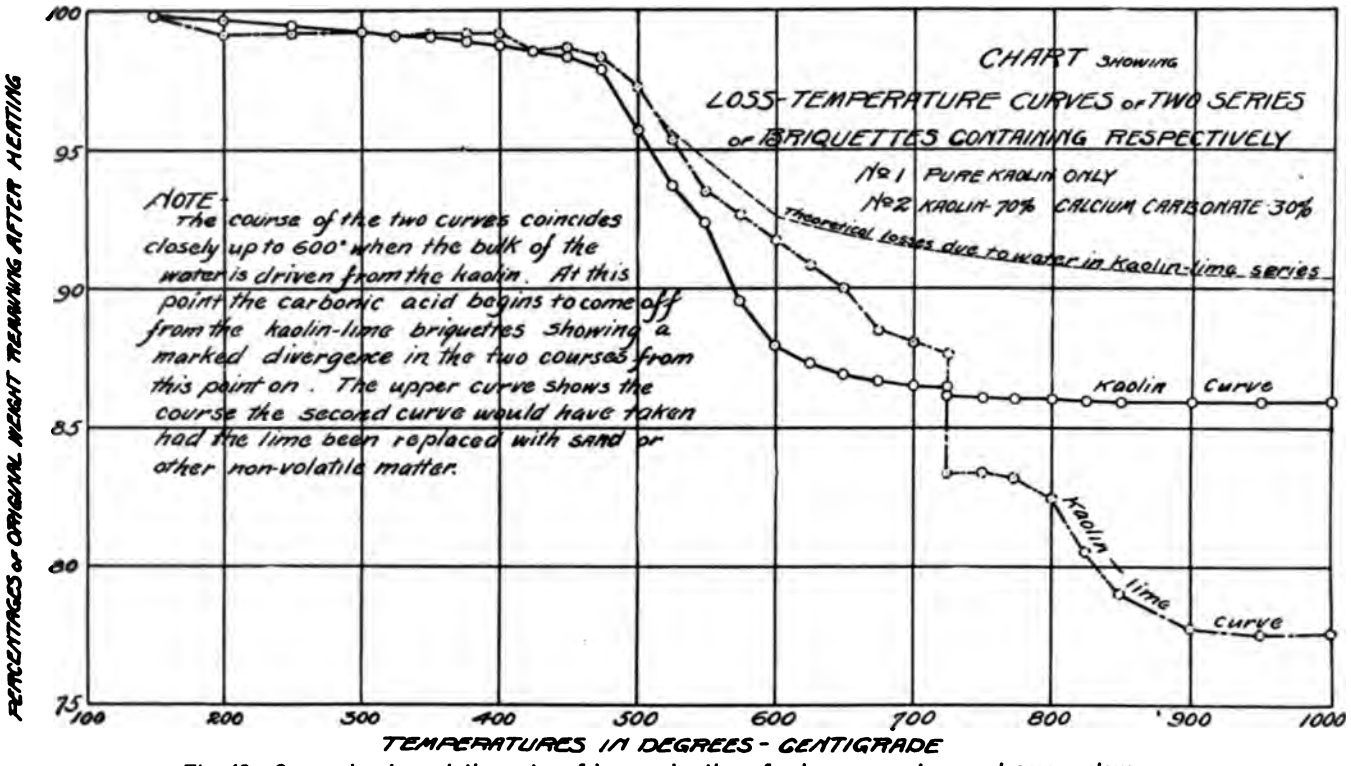
CHART showing
LOSS-TEMPERATURE CURVES of TWO SERIES
of BRIQUETTES CONTAINING RESPECTIVELY
No 1 PURE KAOLIN ONLY
No 2 KAOLIN 70% CALCIUM CARBONATE 30%
NOTE
The course of the two curves coincides closely up to 600° when the bulk of the water is driven from the kaolin. At this point the carbonic acid begins to come off from the kaolin-lime briquettes showing a marked divergence in the two courses from this point on. The upper curve shows the course the second curve would have taken had the lime been replaced with sand or other non-volatile matter.
Theoretical losses due to water in kaolin-lime series
Kaolin Curve
Kaolin - lime curve
PERCENTAGES of ORIGINAL WEIGHT REMAINING AFTER HEATING
100
95
90
85
80
75
100
200
300
400
500
600
700
800
900
1000
TEMPERATURES IN DEGREES - CENTIGRADE

Fig. 18. Curve showing relative rates of loss on heating of calcareous and non-calcareous clays.

a soft marl from near Peebles, Ohio, and was used in three varieties differing slightly in composition. The composition was quite closely:

	Per Cents.
Silica	0.42
Alumina	0.54
Calcium carbonate	55.90
Magnesium carbonate	43.94

The eight dolomitic mixtures were likewise made to correspond to the four formulas:

$$2.5(CaMg)OSiO_2;\ (CaMg)OAl_2O_3$$
$$2.0(CaMg)OSiO_2;\ (CaMg)OAl_2O_3$$
$$1.5(CaMg)OSiO_2;\ (CaMg)OAl_2O_3$$
$$1.0(CaMg)OSiO_2;\ (CaMg)OAl_2O_3$$

These, of course, were prepared as in the lime series.

In the table on page 181 the approximate composition of these cements is shown.

Batch No.	Formula.	Clay Base.	Composition of Ignited Cement.				
			Silica. Per Cent.	Alumina. Per Cent.	Lime. Per Cent.	Magnesia. Per Cent.	Number in Series.
1– 4	$2.5CaOSiO_2$, $CaOAl_2O_3$.....	Kaolin.....	21.14	18.65	59.45	0.2	1
5– 7	" "	Kaolin-quartz mixture.	27.41	8.77	62.88	.....	5
8–11	$2.0CaOSiO_2$, $CaOAl_2O_3$.....	Kaolin.....	23.49	20.68	55.39	0.2	2
12–15	" "	Kaolin-quartz mixture..	30.48	9.84	58.89	.....	6
16–19	$1.5CaOSiO_2$, $CaOAl_2O_3$.....	Kaolin.....	26.18	22.91	50.45	0.2	3
20–23	" "	Kaolin-quartz mixture..	35.73	11.40	52.31	.....	7
24–27	$1.0CaOSiO_2$ $CaOAl_2O_3$.....	Kaolin.....	29.85	25.58	44.54	0.1	4
28–30	" "	Kaolin-quartz mixture..	42.53	13.56	43.64	.....	8
31–34	$2.5(CaMg)OSiO_2$, $(CaMg)OAl_2O_3$	Kaolin.....	23.38	20.18	33.80	22.59	9
35–38	" "	Kaolin-quartz mixture..	28.60	9.57	37.09	24.79	13
39–42	$2.0(CaMg)OSiO_2$, $(CaMg)OAl_2O_3$	Kaolin.....	25.74	22.28	31.18	20.84	10
43–46	" "	Kaolin-quartz mixture..	32.34	10.72	34.13	22.81	14
47–50	$1.5(CaMg)OSiO_2$, $(CaMg)OAl_2O_3$	Kaolin.....	28.92	24.80	27.74	18.54	11
51–54	" "	Kaolin-quartz mixture	37.30	12.14	30.24	20.21	15
55–58	$1.0(CaMg)OSiO_2$, $(CaMg)OAl_2O_3$	Kaolin.....	32.41	27.94	23.70	15.84	12
59–62	" "	Kaolin-quartz mixture..	43.63	14.10	25.30	16.91	16

After being made up, ground and dried, these cements were burnt in large Hessian crucibles in a vertical test kiln of the Ceramic Department at the Ohio State University, the temperatures being determined by means of the Chatelier pyrometer. Contrary to expectations, the tendency to dust at higher temperatures was not marked with most of the cements. At 1250° C., all the cements with kaolin were vitrified or partially fused.

In regard to dusting (batch) numbers 1, 2 and 6 showed this tendency in the most striking manner. The dolomitic cements did not dust at all. In removing the content of the crucible, care was taken to reject all of the material clinging or fused to the sides. The crucibles were removed from the kiln as soon as the desired temperature was reached, being thus cooled very rapidly.

The cements were now ground and made up into briquttes, one cement, one sand, placed under a moist cloth, and when sufficiently hardened were placed in water for 28 days.

The results of the tests are given by the following table:

PURE LIME SERIES.

Number.	Clay base.	Formula of Cement.	Temperature of burning, ° C.	Tensile strength, 1 cement: 1 sand, 28 days in water. Pounds per sq. in.	Remarks.
1	Kaolin.	$(2.5CaO)SiO_2, CaOAl_2O_3$	900	....	Briquettes broke.
2	"	"	1,000	156	Hot and sticky.
3	"	"	1,100	....	Not tested.
4	"	"	1,300	39	Quick setting, dry and crumbly.
5	Kaolin-flint mixture	$(2.5CaO)SiO_2, CaOAl_2O_3$	900	181	
6	"	"	1,000	225	
7	"	"	1,100	145	Hot and sticky.
8	Kaolin.	$(2.0CaO)SiO_2, CaOAl_2O_3$	900	20	Softened.
9	"	"	1,000	183	
10	"	"	1,100	....	Not tested.
11	"	"	1,270	55	Dry and crumbly.
12	Kaolin-flint mixture	$(2.0CaO)SiO_2, CaOAl_2O_3$	900	182	
13	"	"	1,000	218	
14	"	"	1,100	111	Set too rapidly.
15	"	"	1,230	....	Broke up in 2 days.

PURE LIME SERIES—Continued.

Number.	Clay base.	Formula of cement.	Temperature of burning. C°.	Tensile strength, cement; sand 28 days in water. Pounds per sq. in.	Remarks.
16	Kaolin	$(1.5CaO)SiO_2\ CaOAl_2O_3$	900	37	
17	"	"	1,000	108	
18	"	"	1,100	46	Softened.
19	"	"	1,230	....	Broke up.
20	Kaolin-flint mixture	$(1.5CaO)SiO_2\ CaOAl_2O_3$	900	216	
21	"	"	1,000	211	
22	"	"	1,100	208	
23	"	"	1,230	....	Broke up.
24	Kaolin	$(CaO)SiO_2\ CaOAl_2O_3$	900	....	Broke in clip.
25	"	"	1,000	96	
26	"	"	1,100	71	
27	"	"	1,230	....	Broke in 2 days.
28	Kaolin-flint mixture	$(CaO)SiO_2\ CaOAl_2O_3$	900	188	
29	"	"	1,000	166	
30	"	"	1,100	46	
31	Kaolin	$2.5(CaMgO)SiO_2\ (CaMgO)Al_2O_3$	850	261	
32	"	"	950	320	
33	"	"	1,050	148	
34	"	"	1,230	....	Broke up in 3 days.
35	Kaolin-flint mixture	$2.5(CaMgO)SiO_2\ (CaMgO)Al_2O_3$	850	175	
36	"	"	950	235	
37	"	"	1,050	284	
38	"	"	1,230	....	Broke up.
39	Kaolin	$2.0(CaMgO)SiO_2\ (CaMgO)Al_2O_3$	850	82	
40	"	"	950	80	
41	"	"	1,050	....	Softened.
42	"	"	1,230	....	Broke up in 2 days.
43	Kaolin-flint mixture	$2.0(CaMgO)SiO_2\ (CaMgO)Al_2O_3$	850	251	Works up well.
44	"	"	950	256	
45	"	"	1,050	48	

PURE LIME SERIES—Concluded.

Number.	Clay base.	Formula of cement.	Temperature of burning. °C.	Tensile strength. 1 cement; 1 sand. 28 days in water. Pounds per sq. in.	Remarks.
46	"	"	1,250	....	Broke up in 2 days.
47	Kaolin	$1.5(CaMgO)SiO_2 (CaMgO)Al_2O_3$	850	....	Broke in clip.
48	"	"	950	....	"
49	"	"	1,050	....	"
50	"	"	1,250	....	"
51	Kaolin-flint mixture	$1.5(CaMgO)SiO_2 (CaMgO)Al_2O_3$	850	89	
52	"	"	950	324	
53	"	"	1,050	....	Briquettes broke
54	"	"	1,250	....	"
55	Kaolin	$(CaMgO)SiO_2 (CaMgO)Al_2O_3$	850	....	Briquettes broke.
56	"	"	950	....	"
57	"	"	1,050	....	"
58	"	"	1,250	....	Slaked.
59	Kaolin-flint mixture	$(CaMgO)SiO_2 (CaMgO)Al_2O_3$	850	337	
60	"	"	950	313	
61	"	"	1,050	....	Briquettes broke in handling.
62	"	"	1,250	....	"

The following conclusions may be deduced from a study of the above results:

1. The best temperature for burning calcareous Roman cements is 1000° C. Below this temperature hydraulicity is not fully developed, above it a non-hydraulic compound is evidently produced; whether on going still higher hydraulicity is restored has not been determined, but seems doubtful.

2. Roman cements having as a clay base pure kaolin are greatly inferior to cements containing a silicious clay base in each and every case. Whether this inferiority is due to the lack of silica or to the excess of alumina cannot be stated. But this seems to indicate that the hydraulicity of these cements is pozzuolanic in character.

3. The pozzuolanic character is emphasized by the fact that a decrease of as much as 10 per cent. of calcium oxide does not produce

any considerable decrease in tensile strength, indicating that as long as there is sufficient lime to change the quartz to "soluble" silica about the same hydraulicity is maintained. It cannot be said, therefore, that good Roman cements must correspond to a definite formula, as has been claimed by Jex, who lays down as the type formula a compound corresponding to $8CaO3SiO_2Al_2O_3$; which, according to him, hydrates to $3CaSiO_35Ca(OH)_22(Al_2(OH)_3$, thus resulting in 42.4 per cent. of meta-calcium silicate and 57.6 per cent. of calcium nd aluminum hydrates.

4. The proper burning temperature of dolomitic Roman cements is about 950° C. and should be lower rather than higher.

5. Silicious dolomitic cements give rise to greater hydraulicity in every case than those containing pure clay substance as a base.

6. Dolomitic cements show a greater hydraulicity than calcareous cements. Whether or not this is due to a reinforcement of the pozzuolane reaction, by a Sorel cement reaction cannot be said. It is possible that if the $2.5(CaMg)OSiO_2$ cements with the 56 kaolin 44 quartz clay base had been burnt more rapidly up to 1300° it would have shown a reconstruction of hydraulicity, owing to the formation of a vitrified magnesian Portland cement. None of the less basic cements, however, could have shown such a behavior. If it had been still more basic, corresponding, about, to $2.8(CaMg)OSiO_2$ $2(CaMg)OAl_2O_3$ we could predict the formation of a Portland cement and hence a great rise in hydraulic strength with certainty.

Similarly, a Roman cement high in lime, approaching a tri-calcium silicate, would become by vitrification a Portland cement with great increase in strength. This is actually realized in the high calcium natural cements of the Lehigh Valley in Pennsylvania. If the tensile strength of such basic cements, calcareous or magnesian, wereplotted co-ordinate with the temperature of burning, we would have a curve showing two minima and two maxima. The first minimum would of course be due to under burning, the first maximum would be reached by the proper maturing temperatures, 1000° and 950°, respectively; the second minimum would be due to too high a temperature while the body still remains in the earthy condition, but becomes dense, and the second maximum is the result of vitrification, that is, the production of more complex hydraulic compounds.

Gilmore's Work.—This fact was already realized by General Gilmore in his treatise on "Limes, Hydraulic Cements and Mortars," 1870, where he gives, on page 158, curves bringing out this fact. He took Ulster county, N. Y., cement, burnt it at four stages represented by 1, 2, 3, 4, respectively, where 1 stands for underburnt rock, 2 for properly

burnt cement, 3 for over-burning without vitrification, 4 for vitrification. The composition of the stone (layer No. 12) was as follows:

	Per Cents.
Silicious residue	19.64
Alumina	7.52
Ferric oxide	2.38
Calcium carbonate	30.72
Magnesium carbonate	35.10
	95.36

The ordinates represent the breaking weights of rectangular parallelopipeds, 2 inches by 2 inches by 8 inches, the pressure being applied at

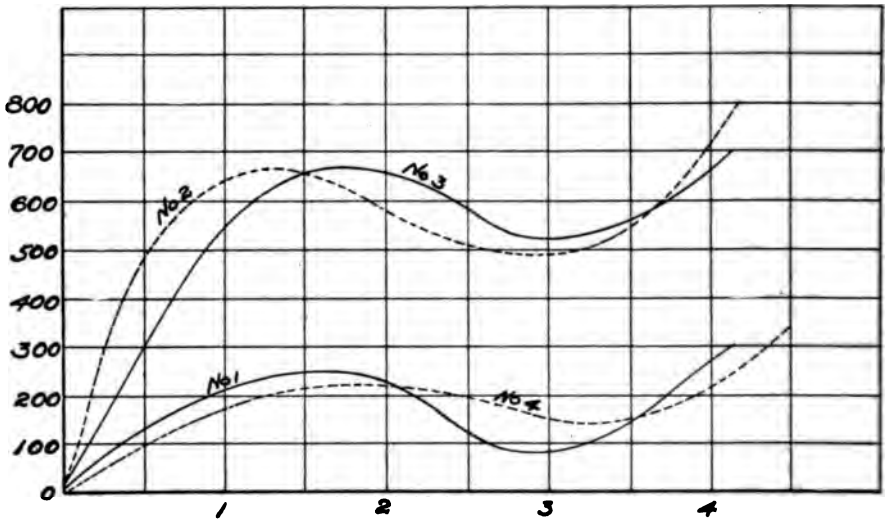

Fig. 19. Gilmore's curves, showing double maxima and minima in strengths of cements by variation in burning temperature.

the middle. Curve No. 1 represents 1 volume cement to 2 volumes sand, age 95 days; No. 2, neat cement, 95 days; No. 3, neat cement, 60 days; No. 4, 1 volume cement to 1 volume sand, 60 days.

The same results are recorded by Feichtinger as having been obtained by Gaetschenberger with dolomitic marl from near Heidelberg.

Summary of the Results.—Summarizing the results in regard to the burning of Roman cements, we can make the following statements:

1st. For Roman cements, high in lime, approaching the tri-calcium silicate and low in magnesia, best burning temeprature is 1000° C. Such stone can be made into Portland cement by vitrification. This cannot be

done successfully, however, with a Roman cement equipment, but requires more elaborate and expensive machinery and kilns.

2nd. Roman cements, lower in lime than 1, and free from magnesia, can only be burnt at 1000° C.

3rd. Roman cements, high in magnesia, should only be burnt at 950°C, as the great strength produced by making a magnesia Portland cement is counterbalanced by the danger of inconstancy in volume due to the two rates of hydration of lime and magnesia, the latter hydrating only after the first has assumed a stony hardness, thus breaking the structure of the cement. In very sandy mortars and some kinds of work they might perhaps be used, but at this stage of our knowledge concerning cements they cannot be considered a safe proposition.

4th. Cements, dolomitic, less basic than the subsilicate, to be burnt only at or about 950°.

These facts are well realized by natural cement manufacturers, who endeavor to burn their cements below the point at which decrease in strength occurs, and this they accomplish by leaving some of the calcium carbonate in dolomitic rocks undecomposed. It is hence unreasonable to demand of Roman cement manufacturers that they produce cement burnt to a point at which all volatile matter is expelled, but, of course, this does not mean that raw rock should be allowed to be ground together with the cement.

Artificial Roman Cement.—The question has been raised as to the feasibility of producing an artificial Roman cement by blending clay and limestone in the proper proportion, burning the mixture to a low temperature, and grinding the resulting soft material to the usual fineness. There is no doubt as to the technical feasibility of this plan, and the large dolomitic limestone deposits of Ohio could thus be utilized without difficulty, but the commercial aspect is not promising, especially since the cost of production of Portland cement is being lowered so decidedly. This plan, however, might be carried out in countries without proper Portland or natural cement materials, but possessing dolomitic limestones.

The Kilns.—The kilns used differ somewhat in size and shape in different localities. In the Louisville district they are cylindrical in shape, consisting of a cylindrical iron shell lined with fire-brick, about 45 feet high, and 16 feet in diameter; in the Rosendale district many kilns are 10 feet in diameter (inside), and about 29 feet high; near Akron, N. Y., the writer saw a kiln oblong in section, 15 feet by 8 feet and 25 feet high. At Milwaukee a kiln is used, 11 feet in diameter (inside), and 36 feet high. In the Rosendale district the kilns usually are built together in a row of masonry braced by heavy timbers and iron rods. All the kilns are narrowed at the bottom to a neck, through which the calcined cement is discharged. The coal, usually anthracite, or a good grade of

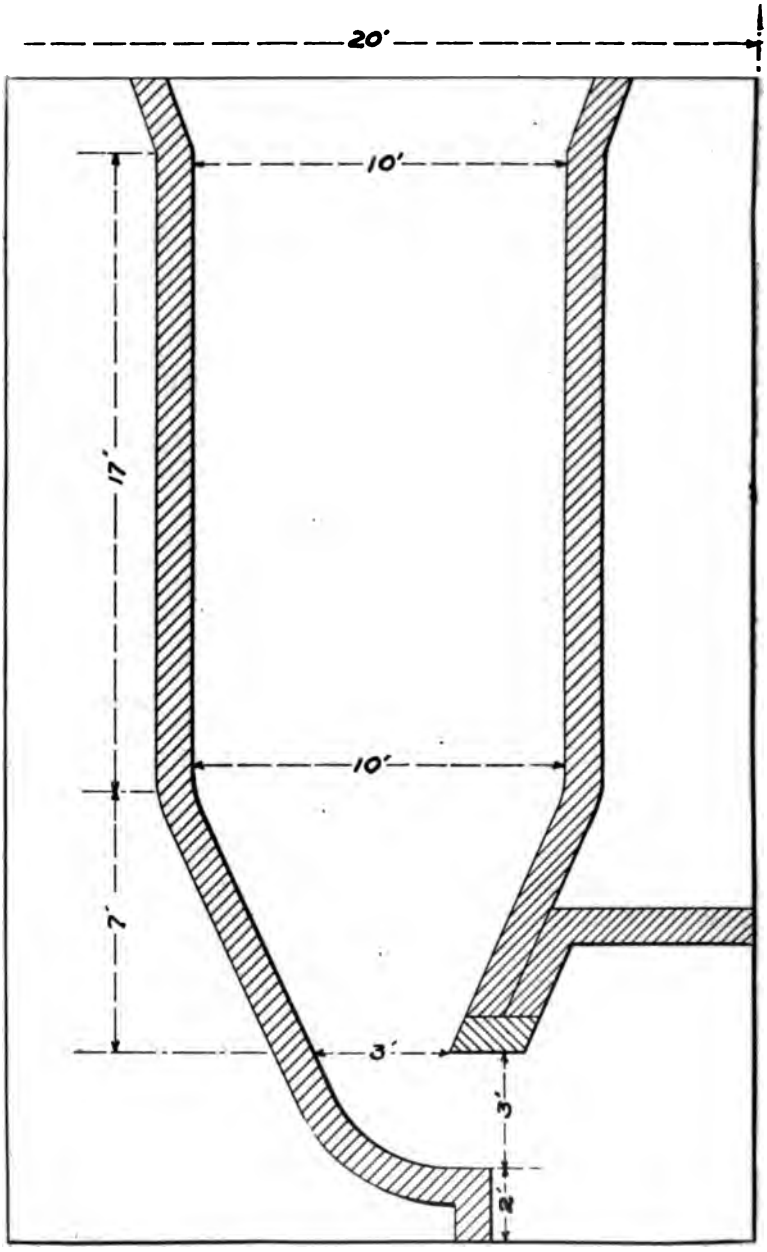

Fig. 20. Cross-section of the type of natural cement kiln in most general use.

bituminous, is charged, together with the stone, in alternate layers. For 100 pounds of stone, about 10 pounds of good anthracite coal is charged; in the plant at New Lisbon, Ohio, it is customary to add sixteen shovels of good bituminous coal to a carload of about 3,500 pounds of stone.

The kilns employed in the natural cement industries have undergone practically no change during the last thirty or forty years, being simply vertical shafts with contracted bottom, of various, but not greatly differing dimensions. All of these kilns are now operated on the continuous plan, since not only the output, but also the quality, of the cement is superior to that burnt in the periodic shaft kiln. The quality of the cement could be further improved by the use of furnaces arranged around the circumference of the kiln, so that the fuel would not need be in contact with the stone and also the distribution of the heat could be effected with much greater efficiency. However, the greater expense of operating the kilns would probably prohibit its use. Such kilns have been tried by American cement makers, and as far as qualitative results are concerned were eminently successful. Some improvements have been made in regard to the distribution of air in the ordinary kiln among which Campbell's grate in the kiln bottom might be mentioned. There is no doubt but that natural cement could be burnt in the rotary kiln with good success, especially since the time of burning would thus be considerably shortened, resulting in a better quality of cement. The fuel consumption would, of course, be greater, but the greater uniformity and quality of the product would compensate to some extent for the waste in fuel. A rotary kiln, of the usual size, 60 feet by 6 feet, should have no difficulty in burning on an average 250 barrels of natural cement per day, as no delay due to "rings" would occur and the lining would not be attacked as vigorously as it is in Portland cement kilns. Obviously the cement rock would have to be reduced to about pea size, at least, before being fed into the kiln.

Rough Grinding.—As usually practiced, the selected burnt rock is sent first to the "cracker" and from there to the millstones. The cracker consists of a frustrum of a cone, made of cast-iron with a chilled shell which revolves within the inverted frustrum of a right hollow cone. Both are provided with corrugations for breaking up the stone. The lower parts of the cones make a smaller angle with the vertical axis than the upper, thus securing a more gradual reduction of the stone. The diameter of the shell is about 15 inches at the top and 6 inches at the bottom. The height is about 18 inches. A cracker of this size will grind enough stone for about 300 barrels per day, making 80 to 85 revolutions. From the cracker the crushed material passes on to the mills. In some plants the crushed stone is screened on the way to the mill, while in others everything goes through the fine grinding machine. An ingenious system of screening has been perfected by Berthellet in which all of the

crushed material makes a complete circuit, the fine material being constantly removed and the coarser particles being even carried along with the fine grindings from the buhr mill, since they insure better working of the screens.

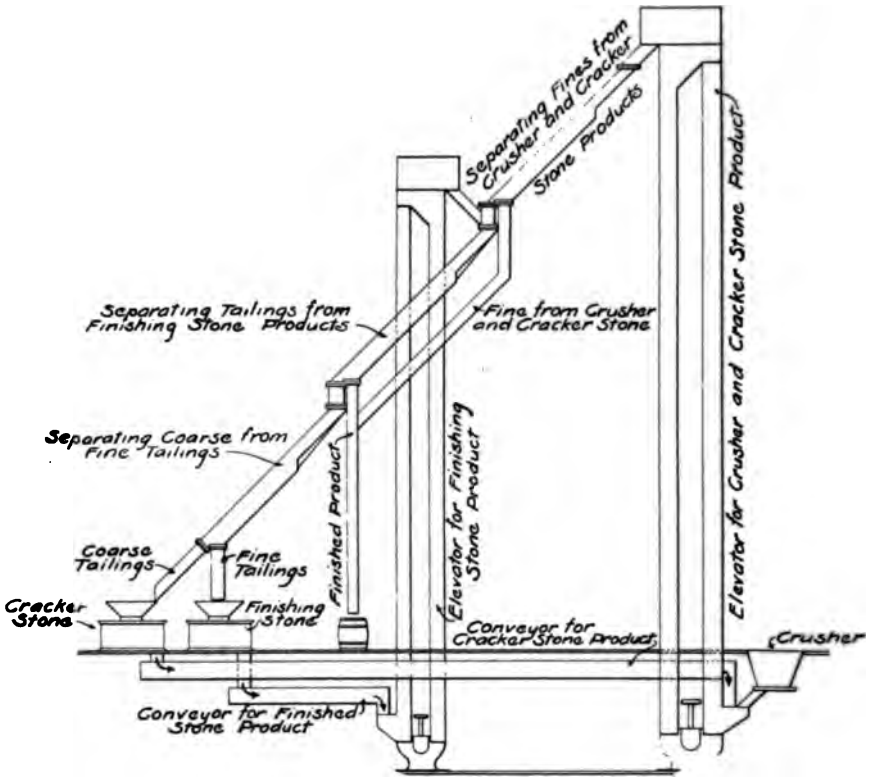
Separating Fines from Crusher and Cracker Stone Products
Separating Tailings from Finishing Stone Products
Fine from Crusher and Cracker Stone
Elevator for Crusher and Cracker Stone Product
Separating Coarse from Fine Tailings
Finished Product
Elevator for Finishing Stone Product
Coarse Tailings
Fine Tailings
Cracker Stone
Finishing Stone
Conveyor for Cracker Stone Product
Crusher
Conveyor for Finished Stone Product

Fig. 21. Berthellet system of screening.

Fine Grinding. —The mill most frequently used is the old-fashioned buhr mill, from 3 to 5 feet in diameter. One of the large size mills will grind about 10 barrels of cement per hour. These mills require, however, frequent dressing, which is equivalent to considerable expenditure of time and money. Emery mills are now being used in considerable numbers, which have proven more efficient, as they need less dressing. A 42 inch emery mill will grind from 18 to 20 barrels of rock per hour, 95 per cent. passing the 100 mesh sieve. The power required is about 15 to 18 horsepower. The grindings from the finishing mill are usually screened and delivered to the hopper, from which chutes take the cement to the packing room. Usually the rock cement is not stored, but shipped at once. This, of course, is a matter depending on the composition of the rock. Very basic cements must be stored.

Some cement makers have adopted the tube mill for fine grinding. Though requiring more power, the tube mill can easily grind 250 barrels and has the advantage of doing away with the screening. It seems that its general adoption would be a progressive step in spite of the greater amount of power required, especially since it eliminates the troublesome attention required in the dressing of stones. The tube mill must invariably be preceded by an intermediate grinding machine, a disintegrator or Kent mill.

Variability of Product.—In the nature of the case the rock cement makers labor under the great disadvantage of being compelled to work with natural materials whose composition cannot be controlled or regulated. If the rock happens to be of the right composition, all is well; if not, nothing can be done. It is idle to claim that these natural variations in composition can be neglected; for poor cement is liable to result, and will reach the market unless its character is discovered by testing. But the limits allowable are quite wide, owing to the pozzuolanic character, and some cements have never given any trouble.

Improvement in Quality by Treatment.—Since our American cement rocks are principally of the mono-silicate type (O.R.1 : 1) and frequently fall below this degree of basicity, and again since the prevailing reaction seems to be pozzuolanic in character, the idea is at once suggested that an addition of dry, hydrated lime might improve many of these cements, just as the hydraulicity of granulated furnace slag is increased by the addition of slaked lime. Following this line of reasoning, the writer made some experiments carried out by burning typical cement rocks obtained from the Rosendale, Louisville and Utica districts and grinding the calcined rock together with dry slaked lime in a ball-mill.

The following results were obtained, the comparisons being made with the identical three samples of cement rock:

Number.	Kind of cement.	Tensile strength in pounds per sq. in. 1: 1, 28 days.	Remarks.
1	Ground rock alone.....	...	Checked and swollen.
2	No. 1 plus 5% lime.....	230	(Burnt too long.)
3	Ground rock.....	135	
4	No. 3 plus 5% lime.....	200	
5	Ground rock.....	100	
6	No. 5 plus 5% lime.....	270	

The rock in each case had been overburned somewhat. But the increase in strength, due to the small amount of dry slaked lime, is very

remarkable, and it might be well for manufacturers to take up this matter, as it might open a way for greatly improving their product. The cost of adding dry slaked lime to the cement is insignificant compared with the results obtained, especially as, in addition, it causes the cement to work much smoother under the trowel. It might be suggested to add the lime when using the cement. Though even this increases the resulting strength, the results are much more striking when the lime is ground together with the cement. Messrs. H. B. Nichols and Ross E. Hamilton, students in the Department of Civil Engineering, Ohio State University, tested Louisville cement by making it up with varying amounts of fat slaked lime and sand in the proportion 1 :2, as shown by the accompanying table:

Louisville cement.	Fat lime. per cent.	Tensile strength 1: 2 after 26 weeks. Pounds per sq. in.
100	..	292
96	4	335
92	8	325
90	10	325
85	15	322
80	20	357
75	25	304
70	30	335
50	50	170

These experimenters, when making up several Portland cements with fat lime, found not only no increase, but at once a decrease in tensile strength with 1 :3 mixtures, just as was to be expected, owing to the fact that Portland cement already has its quota of lime.

Strength of Roman Cements.—In regard to the strength of Roman cements it should be said that in most cases they possess ample crushing strength for all practical purposes, but have two great drawbacks, viz: first, lack of uniformity; second, inconstancy in volume. The greatest difficulty in using Roman cements is their liability to increase in volume, which makes them unsuited for exact work like sidewalks and similar uses. For foundations, especially when used in very sandy mortars, the natural cements answer many purposes very well. At present, with the constantly lowering price of Portland cement, the natural cement industry has a difficult position, which can be improved only by bringing the quality of the rock cements up to the highest possible point.

This means the rejection of unsuited rock based on chemical examination, uniform burning, and fine grinding, together with any other improvements like the addition of dry slaked lime, whenever found beneficial. A great deal of the prejudice against natural cements is based on erroneous conceptions and they are barred frequently from fields in which by virtue of their cheapness they might be used with economy.

In regard to the strength of Roman cements, the following figures might be cited. Tetmayer found the average specific gravity of Swiss Roman cements to be 2.98, and their average strengths as given in table below. These cements are principally calcareous.

Tensile and Crushing Strength of Swiss Roman Cements, According to Tetmayer.

Mixture.	Time in water.	Tensile strength in pounds sq. in.	Crushing strength in pounds sq. in.
Neat	28 days	203	2,347
"	84 "	356	3,871
"	210 "	401	5,600
"	365 "	416	6,676
1: 3	28 days	190	1,717
"	84 "	312	2,884
"	210 "	396	4,025
"	365 "	407	4,517

Standard Test.—With reference to American natural cements, the following minimum and maximum tensile strengths per square inch have been suggested by a committee of the American Society of Civil Engineers:

Neat Cement—One day; one hour, or until set, in air, the rest of the 24 hours in water, from 40 to 80 pounds.

One week; one day in air, six days in water, from 60 pounds to 100 pounds.

One month (28 days); one day in air, 27 days in water, from 100 to 150 pounds.

One year; one day in air, the remainder in water, from 300 to 400 pounds.

Sand Mixtures—1 *cement*: 1 *sand, by weight.*

One week; one day in air, six days in water, 30 to 50 pounds.

One month (28 days); one day in air, 27 days in water, 50 to 80 pounds.

One year; one day in air, the remainder in water, 200 to 300 pounds.

The specific gravity of Roman cements varies so greatly that it cannot be considered a criterion of its value.

NATURAL CEMENTS IN OHIO.

This industry is very insignificant in this State, being represented at present only by one plant in operation, two others being idle. The plant in operation is located at New Lisbon, while the other mills are at Defiance and Bellaire. The mill at New Lisbon is a small plant, having five kilns, of which, however, only two or three are operated at present, having a capacity of from 100 to 150 barrels a day. The mechanical outfit is very simple, consisting of a cracker and buhr mills, one 3 foot buhr mill turning out about 100 barrels a day. A 50 horsepower engine operates the mill. The stone is mined, eight miners and one driver being employed. For each car of 3,500 pounds, 16 shovels of good bituminous coal is added when charging the stone into the kiln. The kilns are about 30 feet high and have an inside diameter of about 10 feet. Three of the kilns are built together in a block, while two of them are iron jacketed and separated. Once a day, in the morning, each kiln in operation is drawn, furnishing about 50 barrels. When operating two kilns, 14 men are employed altogether, eight miners and one driver, two kiln men and three mill men. When running two more kilns, three more men are needed.

The mill at Defiance works the dolomitic rock, whose outcrop forms the bed of the Auglaize River, and is a material high in bituminous matter and pyrites. The latter are especially obnoxious, and form regular bands, which are rejected as much as possible. On burning, the iron sulphide causes the cement to clinker and stick, forming a sponge-like porous mass which is thrown away. The two kilns are cylindrical, 18 feet high, and 6 feet inside diameter, widening out at the bottom so as to minimize sticking as much as possible. Each kiln is fired from two furnaces, a cheap grade of wood having been the fuel used. From each furnace two openings lead into the kiln space. Owing to the fact that the stone is high in bituminous matter, the fuel necessary is small in amount, from one-quarter to one-half cord of wood per day. The chief difficulty is in holding back the burning so as to prevent clinkering and to oxidize the iron pyrites. Sometimes the clinkered cement chokes up the holes leading from the furnaces into the kiln. The stone is drawn at short intervals, every thirty minutes, from five to eight, or even twelve wheelbarrows being obtained. At the same time a corresponding amount of stone is charged on top. The machinery consists of a crusher and a buhr mill, three feet in diameter, which must be dressed every three days. The or-

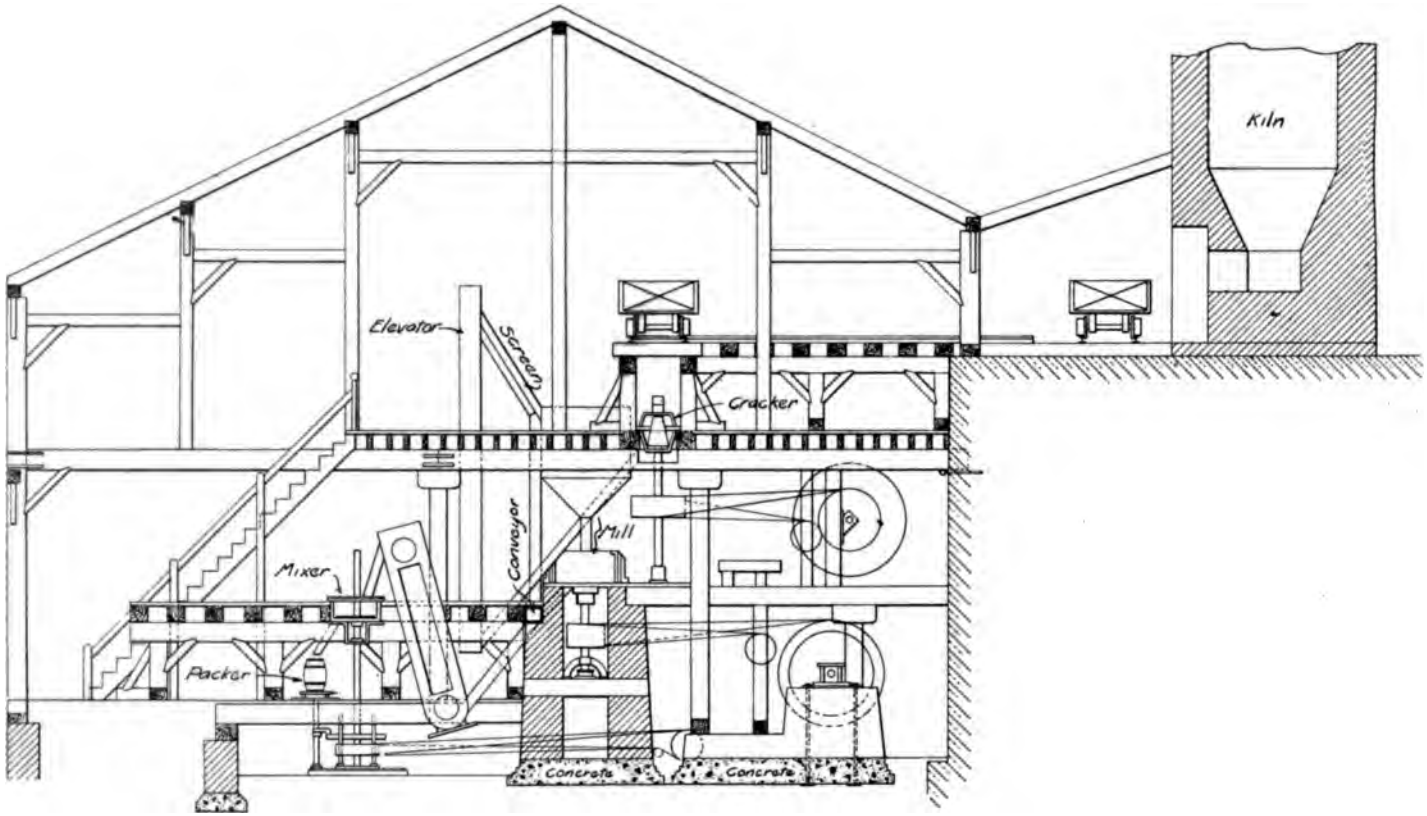

Fig. 22. Cross-section of a natural cement plant.

dinary capacity of the kilns would be 500 barrels, but owning to the troublesome material, it is only about 200 barrels. Sometimes large blocks of clinker must be chiseled out from the kiln, and of course rejected.

Aside from this difficulty, the quality of the cement is good, it having been used successfully in a great many building operations. A peculiar and interesting fact observed is the tendency of the burnt pieces of the stone to split up into small cubes on weathering, affording a striking example of the influence of the crystallization of the pyrites upon the bed structure of the whole deposit.

The maximum thickness of the hydraulic rock is said to be 27 feet the greatest thickness at which it is mined is eight feet, but as a rule about four to five feet are quarried. There are two layers of the stone, which shows a most decided shale structure, and is easily mined. One is a black, the other a gray shale; the first contains the greater amount of bitumen. At this mill, 200 barrels of cement can be produced per day with 11 men, distributed as follows:

1 engineer.
4 kiln men.
1 general help.
2 mill men.
2 quarry men.
1 driver with team.

By using a rotary kiln in which a distinct roasting stage is maintained it is quite probable that this stone could be burnt much more satisfactorily. It is the intention of the proprietor, Mr. Frank Wilhelm, to resume operations on a larger scale.

CHAPTER V.

ON THE NATURE OF PORTLAND CEMENT.

Portland cement is an artificial silicate produced by intimately blending clayey and calcareous materials, burning them to vitrification, and grinding the resultant slag-like mass to a fine powder. This powder, if of the proper composition, will hydrate and harden in water to a stone-like mass, of practically constant volume, which shows considerable tensile and crushing strength and is able to cement together relatively large quantities of sand. In composition it varies between the following limits:

Ingredients.	Per cents.	
	Minimum.	Maximum.
Silica	19	26
Alumina	4	11
Ferric oxide	2	5
Lime	58	67
Magnesia	0	5
Sulphuric acid	0	2.5
Alkalies	0	3.0

The table on page 195 shows the composition of ten American Portland cements of well established reputations:

The average American Portland cement calculates to the formula $1.10CaO$, $0.363SiO_2$, $0.074Al_2O_3$, $0.021Fe_2O_3$ allowing for the presence of 0.83 per cent. of CaO as sulphate. Calculated to the basis of silica equal to unity, we have the general formula: $3.04CaO\ SiO_2$, $0.23Al_2O_3$, $0.058Fe_2O_3$. For purposes of comparison, especially with reference to the study of the clay base of cements, we might calculate still another formula, making the alumina equivalent equal to unity, obtaining: $14.99CaO$, $4.93SiO_2Al_2O_3$, $0.284Fe_2O_3$. The reason for making alumina equal to

Chemical Composition of Standard American Portland Cements.

Number.	Silica.	Alumina.	Ferric Oxide.	Calcium Oxide.	Magnesium Ox.	Alkalies.	Sulphuric Anhydride.	Ratio $\frac{SiO_2}{Al_2O_3}$
				Percentages.				
1	21.22	7.51	3.83	63.75	0.82	not det.	1.58	2.82
2	21.20	7.90	not det.	63.14	2.40	not det.	1.37	2.68
3	21.93	5.98	2.35	62.92	1.10	not det.	1.54	3.67
4	23.36	8.07	4.83	58.93	1.00	0.50	0.85	2.90
5	22.89	8.00	2.44	63.38	2.30	not det.	not det.	2.86
6	22.24	7.26	2.54	64.96	2.26	not det.	0.41	3.07
7	22.04	6.45	3.41	60.92	3.53	not det.	2.25	3.42
8	21.24	7.85	4.14	63.22	0.28	0.68	1.11	2.71
9	20.83	10.58		63.30	2.86	not det.	1.13	.....
10	21.10	8.61	3.21	61.62	2.84	not det.	1.69	2.45
Average	21.76	7.51	3.31	62.61	1.94	not det.	1.19	2.90
For comparison, four well-known German Cements are given:								
11	19.35	7.00	4.50	63.75	.....	not det.	not det.	2.76
12	21.14	6.30	2.50	66.04	1.11	not det.	not det.	3.36
13	22.69	7.30	2.28	62.28	1.08	not det.	not det.	3.10
14	24.90	8.00	3.22	59.38	0.38	not det.	not det.	3.11

No. 11, Dyckerhoff; No. 12, Germania; No. 13, Porta; No. 14, Alsen.

unity is based on the fact that the fundamental formula of clay substance is Al_2O_3, $2SiO_2$, $2H_2O$, showing one molecule of alumina. This last formula therefore tells us that the average clay base corresponds to clay of the formula: Al_2O_3, $0.284Fe_2O_3$, $4.93SiO_2$, showing theoretically 2.93 molecules of free silica under the assumption that none of the alumina is part of feldspathic minerals, an assumption which does not hold for impure clays. The oxygen ratios between the lime, alumina and silica are: 3.04 : 0.69 : 2 making Portland cement equal to a sub-silicate of calcium. These molecular ratios are not exact owing to the presence of varying amounts of coal ash.

We might hence compare Portland cement with a basic slag with which it shows, indeed, many similarities. In nature, we do

not find the exact analogies of Portland cement. From what we know of Portland cement at present we can say that it is, mineralogically speaking, a basic rock and its closest approach in the natural group of rocks is the peridotite group whose principal minerals are olivine, pyroxenes, hornblende and garnet.

REVIEW OF THE INVESTIGATIONS ON THE CONSTITUTION OF PORTLAND CEMENT.

The question as to what Portland cement really is has received a great deal of attention from many investigators, but it seems so far that the closest approach to an accurate conception of the structure of Portland cement has been made by mineralogical examinations while chemical investigations have failed more or less completely. It is interesting to examine the various methods by which investigators have approached the subject and, hence, in the following paragraphs a brief review of some of the work done by various men will be given. Much has also been written by men who base their conclusions on theoretical reasoning entirely. Such contributions are not considered.

The work done in this direction may be classified under several headings indicating the chief method by which it has been endeavored to determine the structure of Portland cement.

1. Mineralogical (microscopic) examination.
2. Study of synthetic mixtures.
3. Study of hydration reactions.
4. Determination of calcium oxide.
5. Study of heat reactions.

Of course, no investigator has confined himself to any single method, but most of the experimenters have paid special attention to one line of attack.

MINERALOGICAL INVESTIGATIONS.

The Work of Chatelier.—The first investigator to approach the subject along these lines was Chatelier,* who attacked the problem in 1887.

In this year he published his classical work on the constitution of Portland cement based on microscopic analysis, in which he states that he found the main constitutents of Portland cement to consist of (1) colorless double-refracting, cubical crystals; (2) between these a darker substance, double-refracting, but without crystalline structure. In addition he found several accessory constitutents.

(a) Slightly yellowish crystals, opaque and showing striation.

(b) Very small crystals with rather strong double-refraction.

(c) Finally, zones of matter without influence on polarized light.

Constitutent No. 1 was called, later, alite; No. 2, celite; a, belite; and b, felite. Chatelier considers the alite as $3CaOSiO_2$, this being the

*Recherches Experimentales Sur la Constitution Des Mortiers Hydrauliques, Annales Des Mines, 1887.

active element of cements, par excellence, which hydrates according to the following reaction:

$$3CaOSiO_2+Aq=CaOSiO_2.5H_2O+2Ca(OH)_2.$$

In addition to this compound, the Portland cement contains a tri-calcic aluminate, which is relatively unstable, but sets rapidly in water, and if present in too large amounts may cause the destruction of the cement. It hydrates according to the reaction:

$$3CaOAl_2O_3+Aq=3CaOAl_2O_3.12H_2O.$$

Chatelier thus considers Portland cement as composed of tri-calcium silicate, with a certain amount of calcium aluminate and ferrate, besides mono and dicalcium silicates. The hydration of the cement he expresses by the two reactions:

$$2(3CaOSiO_2)+9H_2O=2CaOSiO_2.5H_2O+4Ca(OH)_2.$$

Then a reaction takes place between the calcium hydrate, water and calcium aluminate forming a basic calcium aluminate:

$$3CaOAl_2O_3+Ca(OH)_2+11H_2O=4CaOAl_2O_3.12H_2O.$$

The hydrated basic aluminate determines the setting of the cement, while the hardening is fixed by the tri-calcium silicate. Chatelier fixes the amount of lime necessary for Portland cement by the expression:

$$\frac{CaO}{SiO_2-Al_2O_3-Fe_2O_3}>3$$

in which CaO, SiO_2, Al_2O_3, Fe_2O_3 represent the number of equivalents of these substances present. The other limit he fixes by the expression:

$$\frac{CaO}{SiO_2-Al_2O_3-Fe_2O_3}<3$$

The Work of Toernebohm.—Toernebohm practically checked the petrographic work of Chatelier, but arrived at a different composition of the compounds. According to him the Portland cement formula is:

$$X(3CaOSiO_2)-(9CaO2Al_2O_3),$$

in which the value of X fluctuates around 0. This investigator separated the minerals found by means of the Thoulet solution.

The Work of Liamin.—The next worker along petrographic lines was Liamin,* who produced a series of micro photographs of hardened

*Report of the Imperial Russian Technical Society, 1897.

cements showing the interlacing crystals of lime hydrate and lime-alumina silicates forming the hardened cement. Beside these, crystals were found strongly resembling nephrite. But the main active constituent, according to Liamin, is the lime hydrate which forms crystals frequently 1 mm. long. In hardening, the crystals of calcium hydrate and the nephrite-like crystals increase in magnitude. The anhydrous cement contains practically all of the lime combined, the principal mineral present being probably the sub-silicate of lime, which in hydration breaks up into a simpler silicate and calcium hydrate. The two methods of quantitative separation of the different constitutents adopted by Liamin were:

1. Mechanical separation of the ground, hardened, cement by means of solutions of varying specific gravities.

2. Determination of the water of hydration at different temperatures. Liamin made the assumption that the water of hydration of the hydro-silicates leaves at 160° C., while the calcium hydrate loses its water between 450° and 480° C., an assumption by no means proven.

The liquids employed by this investigator in making the mechanical separation of the different minerals of the cement were:

a. Yellow methyl iodide, specific gravity 3.34

b. Benzene, specific gravity 0.89

By means of a mixture of these liquids of 2.3 specific gravity the lime hydrate was washed out and washed free from other constituents by means of the benzene. No trouble was experienced in removing the calcium hydrate, owing to the close specific gravities of the hydrate, 2.18, and of the liquid, 2.3. The amount of calcium hydrates thus obtained he checked by means of the second method. By determining the amount of water expelled at 160° C., and the quantity set free at 480° the amount of free calcium oxide can be calculated, for 18 parts of water correspond to 56 parts of the oxide. If thus

a=total loss of weight on igniting the hardened cement,

b=the loss of hygroscopic water at 100°,

c=the loss of water of hydration at 160°,

d=content of carbon dioxide and,

e=water content of the calcium hydrate,

e=a—(b+c+d), and

$$e\times\frac{\text{molecular wt. calcium hydrate}}{\text{molecular wt. water}}=e\times\frac{74}{18}=4.11\times e=\text{total amount of}$$

calcium oxide in the Portland cement.

Liamin found in 5 Portland cements

after	7 days	hardening from	13.2 to 22.9 per cent. $Ca(OH)_2$.
after	28 days	hardening from	26.3 to 32.3 " " "
after	60 days	hardening from	30.9 to 33.1 " " "
after	180 days	hardening from	31.6 to 33.6 " " "
after	365 days	hardening	32.0 " " "

The two methods of separation appeared to check very well. However, his ingenious and elegant method is open to the objection that neither the water of hydration of the hydrosilicates nor the water of the calcium hydrate has a definite expulsion temperature. In fact, laborious experiments made by the writer for the Ohio Geological Survey have shown that it is impossible to distinguish with any degree of accuracy any particular stage in the dehydration curve. It also requires red heat to expel all of the water of hydration.

The Earlier Work of Richardson.—In 1902 Dr. Clifford Richardson, an American investigator, prepared the tri-calcium silicate synthetically by fusion in the oxy-hydrogen flame, as well as non-dusting dicalcium silicates, both hardening in moist air and water. By means of micro-photographs, he illustrated the crystalline character of Portland cement, and makes the statement that it is a solid solution. This claim has been made by numerous investigators for the last ten years or more, but none of them have, as yet, produced satisfactory physical-chemical data for the purpose of proving this hypothesis beyond all doubt, though at present it would not seem a difficult matter to study the melting points and cooling curves by means of the electric furnace and the optical pyrometer. There is every reason to believe that all slags and slag like materials are solutions, and the work of Howe, Akerman,[1] Vogt,[2] Hofman,[3] Ashley,[4] has furnished important contributory evidence, but we have as yet no right to say that Portland cement is a solid solution, just as the same thing has not been proven for slag and glasses. As has been said, a thorough survey of all the physical properties of pure Portland cements must be made with reference to the specific volume, heat of formation and other physical data made mention of elsewhere.

The Work of Passow.—Dr. Passow, in 1903, examined Portland cement clinker microscopically, and found essentially two predominating constituents, a white crystalline mass, alite, and a dark ground mass or magma. These two constituents are the hydraulic bodies of Portland cement. If, however, a third crystalline substance appears which is characterized by distinct striations, similar to those shown by plagioclase under the microscope, the hydraulicity is impaired in the proportion in which this matter, felite, appears. According to Passow, this offers a ready means of judging the quality of Portland cements, enabling one to detect cements too high in clayey matter; that is, cements approaching too closely the bisilicates.

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[1] *Stahl und Eisen*, 1890, p. 424.
[2] *Betraege zur Kenntniss der Mineralbildung in Schmelzmassen*, Christiania, 1892.
[3] *Transactions Amer. Inst. Min. Eng.* Vol. 29, p. 682.
[4] *Ibid*, Vol. 31, p. 854.

The white crystalline matter, as well as the dark ground mass, can readily be observed in the accompanying micro section made by the writer.

The large crystal seen is a fine specimen of the alite found in normal Portland cements.

Fig. 23. A large crystal of "Alite" in Portland cement clinker (highly magnified).

The Later Work of Richardson.—The most thorough microscopic study of Portland cement is represented by the recent work of Dr. Clifford Richardson,* in which this investigator made an exhaustive experimental series involving various combinations of the mineral constituents of cement. Thus he arrives at the result that pure clinker consists of two distinct solid solutions, alite and celite, the first being tri-calcic aluminate dissolved in tri-calcic silicate, the second di-calcic aluminate dissolved in di-calcic silicate. These, though miscible in the molten state, are not so in the solid form. The limits of the proportions of alite and celite depend on the basicity and the ratio of silicate to aluminate and are roughly 3 to 1 and 6 to 1. This contribution furnishes the most valuable evidence for the solid solution theory as yet produced, but confirmatory proof based on other physical chemical methods of attack, such as the study of cooling curves, is still necessary for the final acceptance of this view.

THE STUDY OF SYNTHETIC COMPOUNDS.

This line of work was begun early in the scientific history of Portland cement. It might well be said that Vicat, in France, was the pioneer in this kind of experimental work on a scientific basis, followed by Rivot, Chatoney and Fremy. In Germany we find Heldt, Fuchs, Schott,

*Address before the Association of Portland Cement Manufacturers, June 15th, 1904.

Michaelis, Feichtinger, Erdmenger, Dyckerhoff, Meyer, Hauenschild and others. Synthetic work of a high order was also done later by Chatelier, mentioned above in connection with his microscopic research. It will be impossible to consider the work of all these investigators, but it is the intention of the writer to cite a few in order to show the way in which the problem has been attacked.

The Work of Schott.—The experiments of Schott,* though not of recent times, deserves recognition inasmuch as he has brought out one or two important facts. He made up a mixture of pure silica, alumina, ferric oxide and calcium carbonate, whose composition after burning was as follows:

Number of mixture	1	2	3	4
Silica	23.8	23.8	23.3	24.3
Alumina	11.4	.....	6.9	6.9
Ferric oxide	.....	11.4	4.7	4.8
Lime	64.8	64.8	65.4	64.1

On burning them to incipient white heat, finely grinding them and making up with water, they all hardened exceedingly well, even No. 2, containing no alumina. On adding 1.5 per cent. of caustic soda to No. 2 it became a brown mass of extraordinary hardness. To cements 3 and 4 still more lime was added, 7.7 and 8 per cent. respectively, whereupon they broke down to a powder, which, however, when again made up with water resumed the hardening process.

Up to about 1885 the various theories advanced defined in a more or less definite way the chemical composition of the cement, but all that practically resulted from these older investigations was the mention of the fact that calcium oxide formed with silica and alumina basic silicates and aluminates which on the addition of water harden by breaking down to simpler compounds and free calcium hydrate. Some of these experimenters also realized that the end products of the hydration reaction are largely colloids.

Various Investigators.—Seftstroem produced fused masses of alumina and lime corresponding to $3CaO.Al_2O_3$, $3CaO.2Al_2O_3$ and $CaO.Al_2O_3$, by burning them in a forge. Winkler produced a rapidly hardening mass, which, however, broke down to a powder, by heating 11 equivalents of lime, 1 equivalent of potash and 4 equivalents of alumina to incipient vitrification. On hardening the mass showed considerable heat-

* "*Dingl. Polyt. Journ.*," 302, 454 and 518.

ing. He also blended 8 equivalents of lime, 1 of potash and 4 of alumina, obtaining a more thoroughly vitrified mass, which, when powdered, hardened strongly in water, and heated but slightly.

Fremy produced aluminates of the composition:

$$3CaOAl_2O_3,\ 2CaOAl_2O_3,\ CaOAl_2O_3,$$

which hardened in water almost instantly. When mixed with sand, these aluminates became almost stone-like in character. Fremy thought the higher the aluminates were burnt the more hydraulic they were. Hence, he advised the burning of Portland cements to as high a temperature as possible, so as to fuse the aluminates and obtain the benefit of their maximum hydraulicity.

Michaelis fused a mass of the formula $3CaOAl_2O_3$ in a gas flame fed with oxygen, and found the powder to harden exceedingly well. The hardened mass was attacked neither by carbon dioxide nor water.

A mixture of $3CaOAl_2O_3$ thus fused and powdered set at once, but softened slowly under water. V. Lieven confirms the hydraulic activity of aluminates, but denies that they contribute to the permanent hardness of cements, since, according to him, they decompose into aluminum hydroxide, calcium hydroxide and calcium carbonate. The products on first hardening are:

$$CaOAl_2O_36H_2O;\ 2CaOAl_2O_35H_2O;\ 3CaOAl_2O_36H_2O.$$

Winkler also experimented with lime and ferric oxide, producing a mixture of eight equivalents of lime, one equivalent of potash and four equivalents of ferric oxide. This resulted after burning in a black, slightly clinkered mass, whose powder heated strongly in water and became friable. Heldt burnt together one equivalent of ferric oxide with eight equivalents of burnt marble, and obtained a vitrified mass, which when powdered and made up with water heated but slightly, and soon broke down to calcium carbonate and ferric oxide.

Michaelis was not at first successful in producing a fused or vitrified mass of calcium and iron, owing to a reduction of the oxide. In an oxidizing flame he obtained the compounds $3CaOFe_2O_3$ and $3CaO2Fe_2O_3$ as fused bodies, which when powdered were red or dark brown in color. Made up with water the $3CaOFe_2O_3$ body heated appreciably, the $3CaO2Fe_2O_3$ compound did not. In air they became tolerably hard, in water they decomposed.

In regard to the function of magnesia, the earlier investigators disagree most decidedly. Fuchs produced a good cement of great hardness from talc; Rivot and Chatoney claim that magnesia behaves analogously to lime, hardening in water like the calcium compounds, but do not advise the use of magnesia, owing to its slowness of hydration.

which interferes with the hydration of any lime present. The alkalies, Fuchs says, have no influence upon the hardening.

The Work of Chatelier.—The synthetic work of Chatelier* may be summarized as follows:

Wollastonite, mono-calcium silicate, which is a mineral found in nature, is not hydraulic. The di-calcium silicate $2CaOSiO_2$, made by heating an intimate mixture of calcium carbonate and quartz, disintegrates spontaneously on cooling, which evidently is due to a molecular change. The tri-calcium silicate, $3CaOSiO_2$, he claims, cannot be obtained by direct synthesis. When made by heating silica with lime, more or less free lime always results. But it may be formed indirectly by crystallization from a magma of more fusible compounds of silica, alumina, lime and iron oxide. This compound is the basis of hydraulic activity in Portland cements. The mono-calcium aluminate $CaOAl_2O_3$ is almost infusible. It shows hydraulic activity. The di-calcium aluminate $(2CaO)Al_2O_3$ is quite fusible and sets when made up with water quite rapidly. It shows, however, a great tendency to disintegrate after hardening.

The tri-calcium aluminate $(3CaO)Al_2O_3$ is decidedly fusible and sets rapidly. The lime-iron compounds all slake with water, and are not hydraulic. According to Chatelier, hardened cement consists of hexagonal crystals of lime hydrate, surrounded by a white mass of needle-shaped hydrous mono-calcium silicate, $CaOSiO_2 2.5H_2O$. The reaction of the hardening process corresponds to the following equation:

$$3CaOSiO_2+xH_2O=2CaO(OH)_2+CaOSiO_2 2.5H_2O.$$

The Work of the Messrs. Newberry.—Of more recent investigations that of S. B. and W. B. Newberry** is one of the most extensive. In their article on "The Constitution of Hydraulic Cement," the title of which, however, is a misnomer, as the constitution of the hydraulic compounds was not touched upon, but only the range of composition was considered, a number of synthetic bodies were prepared. These were made by mixing dry, *without grinding*, almost pure silica alumina and calcium carbonate, moistening, and making into small pieces. These were burnt in a Fletcher pot furnace, fired with gasoline, provided with a Portland cement lining. The temperature reached in this furnace was probably quite high, but it is to be regretted that no attempt was made to measure it by means of Seger cones or other means.

These investigators endeavored to determine the presence of free lime by subjecting the pats made from the cements to the action of steam at 98° C. for four or five hours, after allowing the cement to stand over

Ann. des Mines 1887, 345.

***Journal Society Chemical Industry*, Vol. 16, No. 11.

night. The objection to this test is that it is not an accurate one, and at best but comparative. Messrs. Newberry prepared the following mixtures:

$(2CaO)SiO_2$. The clinker was vitrified, translucent and crystalline. On cooling, fell to a powder. Some of the pieces were quenched in water and these yielded a good cement, which stood the hot test.

$(2.5CaO)SiO_2$. Clinker white, somewhat vitrified. No sign of dusting. Pat showed very good setting quality, hardened slowly in water; decidedly hard after six weeks. Sound in steam test.

$(3CaO)SiO_2$. Clinker shrunken, slightly sintered; no dusting. No heating on hydration. Pat rather soft at seven days, hard at six weeks. Sound in hot test.

$(3.5CaO)SiO_2$. Clinker but slightly sintered; soft; no dusting. Pat set hard, but left glass, curved slightly, and cracked; became hard after several weeks in water. Sound in hot test.

In the following table the results of their tests have been arranged:

Silicates.

Formula.	Ratio, CaO to SiO_2.	Composition.		Pat test.	Hot test.
		CaO.	SiO_2.		
$2CaOSiO_2$	1.85	65.11	34.89	Set hard, hard 7 days, hard 6 weeks.	Sound; on glass hard.
$2.5CaOSiO_2$	2.33	70.00	30.00	Set soft, fair 7 days, hard 6 weeks.	Same.
$3CaOSiO_2$	2.80	73.68	26.32	Set soft, fair 7 days, hard 6 weeks.	Same.
$3.5CaOSiO_2$	3.27	76.56	23.44	Cracked, soft; hard 6 weeks	Same.

The lime alumina compounds were likewise investigated by these experimenters and the following mixtures prepared, which were also burnt at a high temperature:

$(2.0CaO)Al_2O_3$ fused in direct heat, strongly clinkered in crucible; vitrified strongly. Set in a few seconds like plaster. The pat was hard, and on glass after six weeks. Hot test, on glass fairly hard, soft on inside.

$(2.5CaO)Al_2O_3$ fused in direct heat, strongly clinkered in crucible; set quick. Pat off glass in one day; soft and cracked after six weeks.

$(3CaO)Al_2O_3$. Semi-fused in crucible. Powder heats strongly with water. Pat cracked before putting in water. Disintegrated entirely in water. Hot test, curved and cracked soft.

In the following table their results are arranged:

Aluminates.

Formula.	Ratio, CaO to Al_2O_3.	Composition.		Pat test.	Hot test.
		CaO.	Al_2O_3.		
$2.0CaOAl_2O_3$	1.10	52.38	47.62	Set quick, hard, sound six weeks.	Sound; on glass fairly hard.
$2.5CaOAl_2O_3$	1.37	57.85	42.15	Set quick, curved and cracked.	Curved and cracked, soft.
$3.0CaOAl_2O_3$	1.65	62.23	37.77	Set quick, curved and cracked.	Curved and cracked, soft.

The next question examined was whether the cement formula of Chatelier $x[(3CaO)SiO_2]+y[(3CaO)Al_2O_3]$ should not be modified to $x[(3CaO)SiO_2]+y[(2CaO)Al_2O_3]$, since the $(3CaO)Al_2O_3$ showed such inferior qualities. By taking as the clay base, a kaolin and a silicious clay base, and using both formulas, it was found that the formula suggested by Messrs. Newberry produced a much better cement in each case. The effect of ferric oxide was also studied, and it was found that a mixture of $2CaOFe_2O_3$ fused to a black slag which, when ground, was brown in color, did not heat nor set in air or cold water. When placed in steam it hardened rapidly and did not crack on boiling.

A mixture of the formula $(3CaO)SiO_2+(2CaO)Fe_2O_3$, containing 7 per cent. of ferric oxide, gave a cement setting slowly and becoming hard in 28 days. Sound in hot test and on glass. This shows that ferric oxide is able to promote the union of silica and lime similarly to alumina. Some mixtures containing both alumina and iron were prepared in which it was found that perfectly sound and satisfactory cements were produced. In one of these cements no lime was assigned to the ferric oxide; in the other two molecules of lime were reckoned for each molecule of the iron oxide, the percentage of alumina and iron being 4 to 3 respectively. In another mixture, with 4 and 3 per cent. of alumina and iron oxide, but figuring 3 molecules of lime to one of alumina, the resulting cement showed high tensile strength, but failed in the hot test. The alkalies in cement were found to be injurious in effect rather than beneficial.

Magnesium compounds were likewise studied, and it was found that when burnt at the highest white heat of the gas furnace the following results were obtained::

$MgOSiO_2$, hard semi-fused clinker, no hydraulic properties.

$(2MgO)SiO_2$, well sintered, porous clinker; no cement properties.

$(3MgO)SiO_2$, infusible clinker; hardened slowly in moist air, but turned to mud on placing in water.

The conclusions of these writers are summarized by them as follows:

"1. The essential constituents of Portland cement are tri-calcium silicate, with varying proportions of di-calcium aluminate. This composition may therefore be expressed by the formula $x(3CaO\ SiO_2)+y(2CaO.Al_2O_3)$. From this formula it may be calculated that the correct proportion of lime, by weight, in Portland cement is 2.8 times the silica *plus* 1.1 times the alumina.

"2. Iron oxide combines with lime at a high heat and acts like alumina in promoting the combination of silica and lime. For practical purposes, however, the presence of iron oxide in a clay need not be considered in calculating the proportion of lime required.

"3. Alkalies, so far as indicated by the behavior of soda, are of no value in promoting the combination of lime and silica, and probably play no part in the formation of cement.

"4. Magnesia, though possessing marked hydraulic properties when ignited alone, yields no hydraulic products when heated with silica, alumina, or clay, and probably plays no part in the formation of cement. It is incapable of replacing lime in cement mixtures, the composition of which should be calculated on the basis of the lime only, without regard to the magnesia present."

Professor S. B. Newberry repeated part of these experiments in additional work published in 1902* which might be briefly summarized as follows:

He again reports having prepared $3CaOSiO_2$ by mixing the finely ground materials dry, and heating the mixture to a white heat. It does not, however, harden readily. No direct chemical proof of the $3CaOSiO_2$ is given. By fusing the mixture over the oxy-hydrogen blow pipe the $3CaOSiO_2$ was found to be double-refracting, with rectangular cleavage, specific gravity 3.022, is constant in volume, hardens well. A mixture of calcium carbonate and silica, heated for two hours at a red heat, leaves some SiO_2 uncombined unless at least 2½ molecules of CaO to one of SiO_2 are present. At a white heat the mono, di and tri-silicate mixtures become completely combined. The amount of water which a given Portland cement will take up chemically is a function of the mechanical conditions, porosity, etc. It may be as low as 10 or as high as 27 per cent.

On suspending finely divided calcium silicate in sufficient water to dissolve all the lime present, the residues are somewhat indefinite in composition, and continue to lose lime on prolonged action; they have, however, the following composition:

Tri-silicate (not fused), after 29 and 93 days, $3CaO2SiO_23H_2O$.

Tri-silicate (fused), 35 and 228 days, $2CaOSiO_2H_2O$.

The di-silicate (quenched and dusted), did not change in composition and did not hydrate.

Cement and Engineering News, Nov., 1902.

The action of an amount of water insufficient to dissolve all of the lime present (100 cc. to 5g.) on the fused tri-silicate, for thirty days, followed by a treatment with sugar solution for 29 and 186 days, gives a residue approximately $3CaO2SiO_2 3H_2O$ and $3CaO2SiO_2 6H_2O$.

The Work of Zulkowski.—Of special interest are also the results of the synthetic experiments of Zulkowski.* He prepared mixtures of various hydrolites, studied their behavior and found great difficulties in burning them, due to the high heats required and the contamination of the mixtures from the refractory lining. The first mixture prepared was the bi-calcium silicate, which, according to theory, should exist in two modifications, a hydraulic, active one, a basic metasilicate, obtained by rapid cooling or quenching, and an inert body produced on slow cooling. Zulkowski succeeded in producing some of the active variety and found it to harden satisfactorily, setting in three hours and becoming very hard in one month. The water content of the hydrate he found to be 4.06 per cent., and since the theoretical basic meta-calcium silicate contains 9.45 per cent. of water his specimen contained by calculation only $(4.06\times100)\div9.45=42.9$ per cent. of the hydrolite. He did not succeed in producing a purer variety, and hence he resorted to the use of fluxes, using barium, boric acid and fluorspar. Since, however, these additions obscure the real properties of the mixtures, we cannot go further into the discussion of his elaborate results. In regard to the tri-calcium silicate, he denies its existence very strongly, basing his objection on the fact that such a compound would require silicon to have a valency of 6. However, Zulkowski made the attempt to produce it in a Seger kiln, but found that the apparently clinkered product broke down to dust. The burn lasted 10 hours. On making up with water it did not harden.

The dimagnesium meta-silicate produced by Zulkowski on heating for 8 hours at a white heat, set in 2 hours, and after two months in water was of moderate hardness. It was found to contain only 3.31 per cent. of water of hydration, showing an exceedingly slow reaction.

The di-calcium aluminate burnt to vitrification was found to set very rapidly in 2 to 3 minutes, showing distinct heating. After three months in water it showed an enormous hardness. The water of hydration found is shown by the following amounts:

	Per cents.
1 day	12.43
2 days	18.47
3 days	21.64
30 days	24.93

A pat which was two months in water contained 22 per cent. of water of hydration. The mono-calcium aluminate set in 2 minutes,

*Sonderabdruck aus der Zeitschrift, "Die Chemische Industrie." 1901.

and after three months in water showed extreme hardness. Its content of water was found to be 19.87 per cent.

A cement was now prepared with pure kaolin as a basis according to the formula: $2(2CaOSiO_2)+(2CaO)Al_2O_3$.

The composition of this cement was thus:

	Per cent.
Silica	21.12
Alumina	18.61
Lime	58.89
Magnesia and alkalies	1.38

This cement, when powdered, set in 15 minutes, heating somewhat. After 90 minutes it was extremely hard, and after several months in water it was still harder. After 30 days it was found to show 17.05 per cent. of water of hydration. This checked reasonably well with the water of hydration calculated from the two separate mixtures previously prepared, the di-calcium meta-silicate and the di-calcium aluminate. By calculation this cement should contain 16.19 per cent. of water of hydration. This kaolin cement was of a pure white color and might serve as an example of a white cement. A temperature of cone 18 is said to be sufficient for its production.

One of Zulkowski's students also examined a commercial Portland cement of the composition:

	Per cents.
Silica	23.40
Alumina	6.07
Ferric oxide	2.51
Lime	63.87
Magnesia	0.97
Potash	0.80
Soda	1.22
Sulphur trioxide	14.5

which was a cement of excellent quality.

By calculation, according to Zulkowski's views, this cement contains:

61.89 per cent. di-calcium meta-silicate,
12.14 per cent. di-calcium aluminate,
4.35 per cent. di-calcium ferrate,
14.22 per cent. calcium oxide,
0.97 per cent. magnesium oxide.

This ought to contain accordingly 14.67 per cent of water of hydration. On hydration the di-calcium silicate splits off half of its calcium as calcium hydrate, the silica remaining as mono-calcium silicate, the alu-

minate and ferrate lose all of their lime, so that, together with the calcium oxide already free, 43.18 per cent. of calcium hydrate is formed.

In determining the water of hydration there was found after

	Per cent.
1 day	4.30
2 days	6.47
7 days	11.32
21 days	14.44
30 days	14.44

agreeing quite closely with the theory.

Finally Zulkowski pictures the formation of hydraulic cements as follows, assuming that the reaction starts with the ideal clay base, kaolin:

1. On the dehydration of the kaolin and expulsion of carbon dioxide a temporary product is formed by the replacement of the two molecules of water by two molecules of lime, thus, $2SiO_2Al_2O_32CaO$.

2. Addition of another molecule of lime forming a more basic lime-alumina silicate $2(CaOSiO_2)$, $CaOAl_2O_3$. The silicate is not a hydrolite, but the aluminate is, the lime going off as hydrate and the alumina also as hydroxide.

3. With increasing heat both the mono-calcium compounds change to di-calcium silicate and aluminate and all the lime beyond the amount necessary for this purpose remains as free lime.

If for one molecule of pure kaolin in place of the 6 molecules of lime necessary only 5 molecules are taken dusting will take place.

The Work of Meyer.—Equally interesting are the results obtained by Meyer,* who followed in his experiments more closely the work of Chatelier. He prepared cements without alumina, using iron and manganese oxide as fluxes, and had no difficulty in producing tri-calcium silicate, which appeared in colorless crystals as found in ordinary cements. If the temperature is carried too high, white crystals will be found floating in the mass, corresponding to $3CaOSiO_2$. This must be the main hydraulic agent. No aluminates or ferrates are formed, as the alumina and iron must be united with the silicate.

The claim of Zulkowski that the silicate is present as the di-calcium meta-silicate is considered erroneous by Meyer, who claims that this compound could not exist together with free lime. At the same time Meyer does not believe that the tri-calcium silicate can be produced by direct synthesis, but must be prepared by crystallization from a fused magma. The presence of a meta-dicalcium silicate Meyer considers impossible, since, according to him, the tri-calcium silicate hydrates to $2CaOSiO_2H_2O$, which loses half of the fixed water at 160° C., while

*Meyer, *Tonindustrie Ztg.*, No. 144, 1902.

calcium hydrate loses its water at a much higher temperature. The fact that half of the fixed water escapes at 160° C. indicates that the molecule is a double one. The remaining water leaves at a much higher temperature. The process of hydration is represented by the following reaction:

$$2(3CaO)SiO_2+aq.=2[(2CaO)SiO_2H_2O]+2Ca(OH)_2.$$

DETERMINATION OF FREE LIME.

The attempts to accomplish the removal of free lime from the anhydrous as well as the hydrated cement are very numerous indeed, for it is fully realized by every investigator that if this could be accomplished the problem of the constitution of Portland cement would be cleared up. Various reagents for the extraction of the lime have been proposed, and we shall consider the methods proposed briefly in the following paragraphs:

The Work of Rebuffat.—Rebuffat* used for these purposes an aqueous sugar solution, which method, however, has been proven by Feret** to be erroneous, since the solution acts upon and decomposes the basic silicate. Michaelis has raised the same objection and claims that any results based upon such a solution must be wrong. The conclusions of Rebuffat must, hence, be accepted with considerable caution. In brief they are as follows.

He divides cements into two classes, viz:

1. Cements of simple, compact structure, non-crystalline, derived from a mixture of calcium oxide, silicate, and aluminate. These comprise the hydraulic limes and quick setting cements.

2. Cements of crystalline structure derived from a combination of a crystalline mass, consisting of $2CaOSiO_2$ and CaO and the calcium aluminate in various proportions—Portland cements and cements high in silica.

He assumes that the quantitative constitution of the different hydraulic cements after setting is the same. They are formed from a mixture of lime hydrate, hydrated calcium silicate, and hydrated calcium aluminates, with a slight quantity of accessory ingredients. The calcium silicate is the ortho-silicate—$2CaOSiO_2$. The quantity of water of hydration which is absorbed does not exceed 5½ per cent., so that the hydrated compound has the formula $(2CaOSiO_2)_2+H_2O$. In cements high in silicate the presence of a certain quantity of meta-silicate must be accepted. This does not hydrate, but reacts with the aluminates and forms double silicates of calcium and alumina. This fact is important, as it explains the resistance of cements to sea water.

Gaz. Chim. Ital. 1898 and *Tonindustrie Ztg.* 1901, No. 105.

**International Cong. for Testing Building Materials, Paris, 1900.

The calcium aluminate may have one of the following formulas:

$$CaOAl_2O_3$$
$$2CaOAl_2O_3$$
$$3CaOAl_2O_3$$

But unless there is an excess of lime or unless certain conditions of burning prevail, it seems that only $CaOAl_2O_3$ and $2CaOAl_2O_3$ should be considered.

The quantity of water chemically fixed by hydration cannot be determined beforehand. The cements hydrate in different degrees according to whether they harden in pure or lime water. To this are due many peculiarities in setting.

In setting, the calcium ortho-silicate is hydrated to form $2(2CaO\ SiO_2)+H_2O$, which is followed by the hydration of the calcium aluminate. These two reactions take place in different phases for different cements.

With cements of crystalline structure, it must be assumed that the calcium ortho-silicate is found combined with CaO and the calcium aluminate in a definite crystalline condition. Portland cement in the hydrated condition contains but small quantities of calcium aluminate. This explains that in cements of a crystalline character the setting may be caused by the hydration of the calcium ortho-silicate according to the following recation::

$$2(3CaOSiO_2)+3H_2O=2(2CaOSiO_2)H_2O+2Ca(OH)_2.$$

This is associated with the hydration of the aluminate, which in Portland cement consists mainly of mono-calcium aluminate and hydrates with seven molecules of water.

$$CaOAl_2O_3+7H_2O=CaOAl_2O_37H_2O.$$

Rebuffat found that all the water of crystallization does not become free at low heat, but part is expelled at a bright red heat.

Other Investigators.—Dr. Tomei[1] treated hardened cement with an aqueous solution of ammonium chloride and found that the amount of lime thus dissolved decreased in amount after some time. He concluded from his experiments that the stability of the lime compounds increases with time, and that part of the silica from the sand of the mortar enters into combination with the lime.

In 1895, A. Hauenschild[2] treated a number of hydraulic cements with various solutions of ammonium salts and found that the salts did not permit of an exact determination of the lime compounds.

[1] *Tonindustrie Ztg* 1895, p. 177.
[2] *Ibid*, 1895, p 239.

B. Steuer[3] allowed hydrogen sulphide to act upon water in which finely powdered Portland cement had been poured. In this manner he extracted 44 per cent. of calcium oxide which he considered free lime, while the residue corresponded to the formula $CaOSiO_2$.

S. Wormser and O. Spanjer[4] used as reagent for the solution of free lime an alcoholic solution of aluminum chloride. They claimed to have proven that this solution (1 g. in 100 cc. absolute alcohol) does not decompose the silicates, but dissolves only free lime. The per cent. of CaO found to go in solution as such was 25, while in addition 20 per cent. of lime was found present as a highly basic silicate. They calculated, by means of their method, a content of 26.6 per cent. of free lime, and 18.65 per cent. of CaO, combined with 6.15 per cent. silica.

Dr. Hart* in the same year, by means of a 10 per cent. alcoholic iodine solution, found, he claims, 30.34 per cent. of free vitrified calcium oxide in Portland cement; the balance of the cement material he considers as ballast, as slag which does not harden; on hydrating, this vitrified lime hardens under water. He cites this free lime as a fine example of a body whose chemical energy is manifested, not by a thermal reaction, but by a mechanical development of energy. The reason why so much free calcium oxide is not injurious to the cement, he explains by saying that this lime is vitrified and crystalline. Vitrified, crystalline calcium oxide and the amorphous lime, though not distinguished analytically, are different physically. This argument is open to many objections, whose discussion here would lead too far.

HEAT REACTIONS.

Dr. Hart's work was supplemented, however, by thermo-chemical experiments, in which he determined the heats of neutralization of wollastonite $CaOSiO_2$, artificial $CaOSiO_2$, $2CaOSiO_2$, $3CaOSiO_2$, $CaOAl_2O_3$, $2CaOAl_2O_3$, $3CaOAl_2O_3$. He determined the heats evolved for the anhydrous cement as well as for the hydrated and dehydrated cement which had been allowed to harden. The heat of neutralization of the hardened, not dehydrated cement should be higher than that of the clinker, since the former contains a considerable amount of free calcium hydrate. In Portland cement the heat of neutralization is lowered on hydration, while the heat evolved by the dehydrated cement is almost equal to that of the clinker. From this Dr. Hart concludes that from 30 to 34 per cent. of free lime must be present in cement.

[3] *Ibid*, 1899, p. 604.
[4] *Ibid*, p. 1785.
* *Tonindustrie Ztg.* pages 650, 770, 853, 1899; 1900, p. 188.

Dr. Hart gives the heats of neutralization of the various silicates in the following table:

	As clinker.	Hydrated after 28 days.	Dehydrated.
	Calories.	Calories.	Calories.
Wollastonite	13.0	....	....
Artificial $CaOSiO_2$	234.7	187.5	....
$2CaOSiO_2$	325.0	326.0	327.3
$3CaOSiO_2$	270.1	266.0	276.5
$CaOAl_2O_3$	41.4	172.7	238.7
$2CaOAl_2O_3$	201.0	240.2	356.6
$3CaOAl_2O_3$	428.2	266.6	....

The question of whether Portland cement consists of compounds of silica with lime or whether it is simply a colloid mixture of decomposed clay and lime was attacked by Dr. W. Ostwald* from the thermo-chemical standpoint by determining the heats of solution in hydrochloric acid (5 grams cement in 500 cc. acid, specific gravity 1.06) using a beaker calorimeter. His results have shown that Portland cement must consist essentially of compounds of lime and the constituents of clay.

Another interesting more recent investigation was carried on by W. Richter** who found that Portland cement did not react with phenol-phtalein, but did as soon as ignited calcium oxide was added. The latter did not slake like ordinary lime, but broke down to a granular powder. With water the ignited lime set like cement and showed but a slight rise in temperature; it stood the boiling test and reacted with phenol-phtalein. Richter concludes, that all the lime in cement is combined. He claims that there can be no aluminate of lime,as calcium aluminates were found to react with phenol-phtalein. He further prepared a tri-calcium silicate not reacting with phenol-phtalein. The boiling test he does not consider a sufficient criterion for the presence of free lime. The di-calcium silicate he found to possess slight cementing qualities, but it did not stand the boiling test. On grinding the di-calcium silicate with crystalline calcium oxide, a cement was obtained which hardened like a tri-calcium silicate cement. Richter thinks that the hydration reaction proceeds as follows:

$$3CaOSiO_2+H_2O=2CaOSiO_2+Ca(OH)_2.$$

$$2CaOSiO_2+Ca(OH)_2+H_2O=CaOSiO_2+2Ca(OH)_2.$$

In 1899 Dr. Michaelis* published a startling theory which contradicted all the previous assumptions. He claimed that the hydraulic hardening is a combination of chemical and physical processes. For

Tonindustrie Zeitung, 1888, No. 46.
Ibid, 1903, No. 120.

the main constituent, the hydro-silicate of lime crystallization cannot be proven notwithstanding the claims of Chatelier and others. The process of hardening depends upon an increase in volume on the part of some of its constituents, or the formation of gelatinous silicic acid. On letting a large quantity of water act on Portland cement, the volume of the latter is changed to a colloid mass occupying 33 times the original volume. On treating cement with lime water, the volume is increased 21 times. Even quartz, when treated with milk of lime, is converted into the colloid variety in which it is greatly increased in volume. The same is true of alumina and iron. Michaelis cites the manufacture of sand brick, by the action of calcium hydrate on crystalline silica as a proof of his theory. His claims, however, have found no approval by most of the cement chemists and investigators.

Of late, since the study of colloids has assumed new importance, his claims deserve more attention than they have received so far. It cannot be denied that colloidal conditions have something to do with the hydration and hardening of cements.

SUMMARY OF THE CONTENDING VIEWS.

It might seem difficult to draw general conclusions from the array of theories presented to the reader in the foregoing paragraphs, but the conditions are not as complex as they seem if we put our main reliance on microscopic evidence and do not attempt to write precise structural formulas. Portland cements are basic slags produced by vitrification, belonging to the subsilicate group, with the tri-calcium silicate as the main hydraulic factor, assisted by certain calcium alumina compounds which are spinel-like in character or more basic. The main silicate crystallizes out from a more fusible magma, enough of which must be present to produce solution, just as in a porcelain body the fluxes, feldspar and lime have the power to bring into fusion comparatively large quantities of the refractory materials, like kaolin and flint. The percentage composition of the cement requires certain, but by no means narrow, limits of lime and silica, in order to produce a sufficient amount of hydrolite, yet not too much, as otherwise the cement would require too high a temperature for vitrification, since not enough of the magma could be produced at lower temperatures. In nature the only mineral we know as approaching the type of the sub-silicate of an alkaline earth is chondrodite, $Mg_8Si_3O_{14}$, which, however, invariably carries iron and fluorine.

The different stages of the Portland cement reaction may be illustrated by considering the components of the raw mixture. It is made up of calcium carbonate, clay substance, quartz (more or less fine), feldspathic and iron carrying minerals, like mica, augite, hornblende, etc.

1. At about 900° C. the chemical water of the clay substance is expelled as well as the carbon dioxide of the calcium carbonate.

2. At the same temperature the chemical water is replaced by lime forming with the clay substance Al_2O_3, $2SiO_2$ $2CaO$.

Ton. Ztg., 1899, p. 785.

3. At about 1000° C. lime combines with the fine grained free silica, leaving, however, much free lime in excess. The mass now is porous, and when made up with water takes up the latter eagerly by capillary attraction, so that the hydration takes place easily. We now have virtually a Roman cement, setting rapidly and corresponding to the first hydraulic maximum of the natural cement curve. This reaction is essentially pozzuolanic in character.

4. Rising beyond 1000° up to 1100° or higher, the fluxing constituents begin to act, consolidating the mass, more free silica is taken up by the lime, so that we have probably compounds corresponding to the bicalcium silicates. The hydraulicity has been largely destroyed; second minimum of Roman cement curve.

5. As the temperature rises still higher between 1200° and 1450°, depending on the amount of fluxing materials present, vitrification takes place rapidly within a short temperature interval and an exothermic reaction takes place, corresponding to the production of the subsilicate. We may represent this process to ourselves by supposing the fusion of an iron—alumina—calcium silicate which dissolves more and more lime until the basic silicate crystallizes out on cooling. Like all calcareous bodies the magma fuses with great rapidity, accounting thus for the short time required for the operation. The amount of heat evolved in the reaction has as yet not been calculated accurately, which may be readily understood considering the great experimental difficulties. We can readily understand that the clay substance and feldspathic matter enter readily into the reaction, but the combination between the quartz and lime is not so easily accomplished.

RESEARCHES MADE BY THE WRITER.

For the purpose of observing just how the lime combines with the quartz, and at what temperatures, mixtures of silica and calcium carbonate were ground together intimately, burnt in a dental furnace, fired with gasoline gas and the temperature measured by means of the Chatelier pyrometer. The resulting products were sealed in perfectly dry bottles and the heats of hydration determined by means of the calorimeter. This instrument, as shown by the cut (Figure 21), was made at the laboratory and served the purpose for which it was intended quite well. The thermometer, divided into 1-50th of a degree Centigrade, could be read without difficulty accurate to 1-100th by means of a small telescope. The thermometer was calibrated and the water equivalent of the instrument calculated repeatedly. The stirrer consisted of a thick copper wire with a ring at the lower end, a vertical motion being imparted to it by means of a string running over a pulley. Though the construction of the apparatus is open to several criticisms, it nevertheless, on testing, gave close results with standard thermal determinations, showing an accuracy beyond that really needed in this work, inasmuch as the influences tending to produce irregularities during the burning were far more numerous. The corrections made for radiation were carried out according to the

method given in "Physical-Chemical Measurements" by Ostwald and Luther. No correction was made for heats of solution. The samples, having been ground in a porcelain ball-mill, were burnt in a Denver white-clay crucible. The amount of sample used varied from three to five

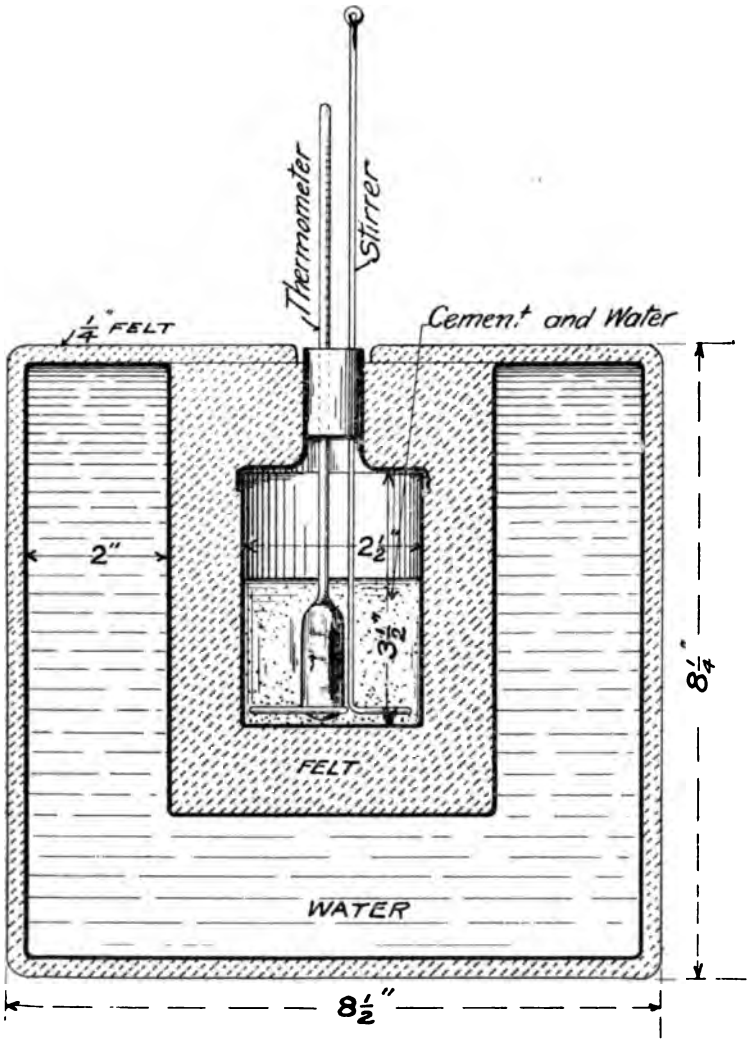

Fig. 24. Calorimeter, for measuring heats of hydration of cements.

grams, and an excess of water was used, 100 cc. The calorimetric work was carried on in a basement room, excessive variations in temperature being thus avoided. Whenever any result was doubtful, a check determination was made.

The ground quartz (flint) showed the following mechanical analysis:

	Per cent.
Residue on 120 mesh sieve	1.40
Residue on 150 mesh sieve	2.36
Residue on 200 mesh sieve	7.06

Grains, average diameter 0.00211 inch	24.74
Grains, average diameter 0.00086 inch	17.84
Grains, average diameter 0.00041 inch	9.30
Dust below these sizes	43.30

The results of these experiments are given in the table below. It was a disappointment to find the results were not as concordant as would be desired, but showed variations that cannot be explained satisfactorily. This was the more annoying since considerable work and time was given to this investigation.

Formula of mixtures.	Calcium oxide per cent.	Silica per cent.	Temperature of burn °C.	Calories per gram.	Equivalents of calcium oxide "uncombined."	Approximate formula of "combined" lime compound.
$1.0CaOSiO_2$	48.27	51.72	600	....	....	
"	....	....	700	2.98	....	
"	....	....	800	1.70	....	
"	....	....	900	7.34	....	
"	....	....	1,000	19.85	0.02	$0.98CaOSiO_2$
"	....	....	1,170	2.76	....	$CaOSiO_2$
$1.5CaOSiO_2$	58.34	41.66	700	10.71	....	
"	....	....	800	15.08	....	
"	....	....	900	67.88	....	
"	....	....	1,000	57.56	0.48	$1.02CaOSiO_2$
"	....	....	1,100	2.76	0.03	$1.47CaOSiO_2$
"	....	....	1,170	1.19	....	$1.50CaOSiO_2$
$2.0CaOSiO_2$	65.11	34.88	700	1.59	....	
"	....	....	800	50.00	....	
"	....	....	900	30.37	....	
"	....	....	1,000	2.50	....	$1.97CaOSiO_2$
"	....	....	1,100	1.20	0.03	$2CaOSiO_2$
"	....	....	1,170	0.79	....	$2CaOSiO_2$
$2.5CaOSiO_2$	70.00	30.00	700	7.54	....	
"	....	....	900	29.37	....	
"	....	....	1,000	73.46	0.95	$1.55CaOSiO_2$
"	....	....	1,100	14.26	0.19	$2.31CaOSiO_2$
"	....	....	1,170	6.80	0.09	$2.41CaOSiO_2$

It is quite evident from the results obtained in this work as well as from other considerations that the heat of hydration of the calcium oxide present in these silicates cannot be used to approximate the amount of uncombined lime. In some manner the lime becomes "dead" burnt and does not hydrate as we should expect, analogous to the "dead" burnt limes in which a few per cent. of silica seem to take away from the time its tendency to slake rapidly. The modus operandi of this process cannot be followed without further investigation. The method proposed by some to determine the lime content of a limestone by igniting it and determining its hydration value hence does not promise to be a satisfactory test. In this connection it might be noted that cements with a silicious clay base, though very high in lime, show but a low heat of hydration. One fact, at least, was brought out quite clearly, namely, that silica does lower the temperature of the decomposition of calcium carbonate quite decidedly.

For purposes of comparison it might be well to quote the heats of hydration obtained by heating a crystalline limestone, 99.5 per cent. calcium carbonate, at different temperatures:

Temperature.	800° C.	900° C.	950° C.	1000° C.	1050° C.	1100° C.	1200° C.
Calories per gram...	34	175	257	260	252	254	247

In addition, these silicates were made up in water and allowed to harden in moist air for forty days, but practically all of them possessed but slight cementing qualities. In water most of them showed but a superficial hardness. Another experiment was decided upon in endeavoring to ascertain something in regard to the attack of lime on free silica. This was carried out by grinding together finely ground quartz, the same which was used in the preceding experiments in the proportion of $0.25CaOSiO_2$, = 18.9 parts of calcium oxide, and 81 parts of silica, igniting the mixture at different temperatures, and determining the residue, insoluble in hydrochloric acid and sodium carbonate solution. It was thought that in this way the lime was bound to come in contact with all the silica it could combine with at the different temperatures. These results are shown in the following tabulation:

Temperature °C.	Per cent. soluble silica.	Per cent. available CaO.	Sum of per cents. soluble silica plus available calcium oxide.	Per cent. carbon dioxide.	Formula.
800	5.94	8.94	14.88	6.60	$CaO, 0.7SiO_2$
900	6.44	16.40	22.84	1.30	$CaO, 0.36SiO_2$
1,100	17.11	18.04	35.15	....	$CaO, 0.877SiO_2$
1,200	22.10	18.04	40.14	....	$CaO, 1.14SiO_2$
1,300	22.73	18.04	40.77	....	$CaO, 1.18SiO_2$

At 800° apparently all of the free calcium oxide has combined with silica, while at 900° there is evidently some lime uncombined, so that the formula appears distorted. It is evident that the lime has united with no less silica than at 800°, but more calcium oxide is available than at the latter temperature. This is indicated also by the decided caustic property of this mixture. The best index of the activity of the lime is the amount of silica rendered soluble, especially if for 800° and 900° the carbon dioxide is eliminated by calculation which will make the soluble silica 6.36 and 6.52 per cent. respectively. The mixtures at 800° and 900° showed caustic properties, especially the 900° sample, while those of the other samples were lumpy and not noticeably caustic.

It is quite evident that the action of lime upon finely ground free silica is reasonably well represented by these experiments, and it appears that at the highest temperature employed, 1300° C., less than one molecule of lime is required to render soluble or available for combination one molecule of free silica, the proportion being 0.847 molecule of calcium oxide to one molecule of silica. This throws additional light on the Roman cement reaction, and explains why such cements may be so low in lime, the function of the latter being simply the "unlocking" of the inert quartz, and the work also indicates that there should be no difficulty in assimilating the quartz of clays, provided the latter is ground fine enough, so that it is not absolutely necessary to depend upon naturally fine clays. The practice of shipping naturally fine clays considerable distances is hence not a necessity, if sand or sandstone in any shape is available. On the other hand it encourages the use of silicious clays in preference to clays comparatively high in alumina.

It must also be realized that in a cement the attack of lime on silica is much more vigorous owing to the formation of a more fusible calcareous magma in which silica is bound to be quite soluble.

CHAPTER VI.

THE COMPOUNDING OF PORTLAND CEMENT MIXTURES.

In the selection of the raw materials the following factors must be considered:

THE CLAYS.

1. The clay must have a percentage ratio of silica to alumina of from 3:1 to 4:1. A clay should be found, if possible, which is naturally fine; but if such a material cannot be found, either a coarse clay of the proper composition must be selected and ground fine, or an addition of ground sand or sandstone must be given a more aluminous but otherwise suitable clay.

In examining many Portland cements this point seems to be the chief difficulty with a number of brands. Owing to the high content of alumina, the cement not only sets too fast, but also shows an inherent weakness. Matters are made still worse by the addition of gypsum, which is a grave source of deleterious influences. At the same time, the clay should not be too silicious, but should lie between the above limits. The sum of the silica and alumina percentages in the hydrous clay should not exceed 87 per cent., thus leaving at least 13 per cent. for combined water and fluxes like ferric oxide, potash and soda.

2. The clay must not contain so much magnesia that the magnesia content of the cement rises above 3 per cent.

3. The clay should contain at least 3 per cent of ferric oxide, but not sufficient to raise the ferric oxide content of the cement over 4 per cent.

4. The clay should be low in sulphur and should not contain more than 1 per cent. of sulphur in any form.

5. The material should be free from any irregularly distributed matter, be it concretionary nodules of ferrous carbonate, calcium carbonate as found in the older sedimentary clays, or lumps of these or similar minerals as found in glacial clays.

Examples of how these considerations are neglected might be cited in considerable number, it having been the writer's task to examine numerous Portland cements. In one case a new plant used a clay of the following composition for its clay base:

	Per cent.
Silica	63.26
Alumina	22.70
Ferric oxide	5.20
Loss on ignition	6.52
	97.68

Ratio SiO_2 : Al_2O_3 : : 2.78 : 1

This mill was in operation for a number of months, but did not succeed in burning satisfactory cement. The heavy financial losses caused the plant to pass into other hands. There is no reason whatever to believe why, with an addition of free silica in some shape, the clay would not have produced a good cement.

Professor Edward Orton, Jr., in investigating certain limestone materials for Portland cement purposes found that the alumina was already high enough, while the silica required an increase. This he introduced in the form of finely ground sandstone, instead of the clay usually employed. The cements resulting from this mixture proved slow setting, requiring no addition of gypsum, but after 28 days showed an extraordinary strength, about 20 per cent higher than the best commercial cements.

Blaese* was compelled to work a clay of the composition:

	Per cent.
Silica	58.19
Alumina and ferric oxide	26.11
Lime	0.78
Magnesia	2.41
Loss on ignition	6.69
	94.18

The cement in spite of an addition of 2 per cent. of gypsum set in 2 to 3 minutes and showed decided "blowing" tendencies, so much, in fact, that barrels of cement were bursted, due to the expansion, in spite of the fact that a series of compositions was made so as to determine the best mixture. In this difficulty, this chemist added sea sand to the clay and succeeded in producing a cement of excellent quality. However, it is interesting to note that an addition of 0.5 per cent. of fluorspar to the raw mix also produced a good cement. This last fact does not help out the statement made above nor does it tend to refute it.

Prof. E. D. Campbell,** of the University of Michigan, has likewise found that lean clays, high in silica, are safer than aluminous clays.

In examining a clay analysis it is always to be recommended that the formula be calculated from it on the basis that alumina is taken as unity.

Tonindustrie Ztg. 1896, No. I.

**Journal Amer. Chem. Society*, 1902, No. 10.

In this manner the mineral character of the clay becomes at once apparent. This, of course, is done by dividing the percentages of the constituents, silica, alumina, ferric oxide, lime and magnesia by the respective molecular weights, and then dividing each quotient thus obtained by the alumina quotient. This will make the alumina equivalent equal to unity.

A clay of the composition:

	Per cents.
Silica	63.73
Alumina	17.17
Ferric oxide	5.85
Lime	0.58
Magnesia	0.97
Potash	2.33
Soda	0.67
Combined water	4.90
	94.00

would thus have a formula corresponding to:

$$\left.\begin{matrix} 0.21KNaO \\ 0.20CaMgO \end{matrix}\right\} \left\{\begin{matrix} 1.0Al_2O_3 \\ 0.22Fe_2O_3 \end{matrix}\right\} 6.32SiO_2.$$

This tells us at once that this clay contains at least 4.32 molecules of free silica. Since the limits of silica to alumina given are 3:1 and 4:1 expressed in parts by weight, or percentages, they can also be expressed in molecular proportions in which the limits are: 5 molecules of silica to 1 of alumina and 6.66 silica to 1 alumina.

The limit set for the sum of the silica and alumina provides for fluxes which are necessary to promote the formation of an easily fusible magma and especially for a liberal amount of ferric oxide. The lower the fusing point of this magma, the more readily will the cement mixture vitrify and the lower will be the cost of burning.

As to the magnesia limit, much has been claimed pro and con, and the last word in this matter has not been said. Dyckerhoff probably has done more work than any one else in this respect, and it is his opinion that magnesia is a dangerous ingredient, if present in large quantities, owing to its slower hydration, which takes place when the calcium compounds have already become hardened, thus causing cement to expand unduly and destroying its structure more or less.

Ferric oxide, if present in not too great a quantity, is a desirable fluxing ingredient. Sulphur compounds are undesirable, since they form either compounds of lower oxidation, which on the hydration of the cement oxidize to sulphates with increase in volume, or, if already oxidized or oxidized in the kiln, take away as much lime from the silica as is necessary to form calcium sulphate, thus lowering the content of available lime. Calcium sulphate in itself is an undesirable ingredient

owing to its solubility in water, 1 part of anhydrous sulphate being soluble in 488 parts of water at 18° C. This apparently slight solubility after all is not to be neglected, especially since its solubility is increased most decidedly by the presence of other salts like sodium chloride, calcium chloride, etc. Thus at 21.5° C. a 3.5 per cent. solution of sodium chloride can dissolve 0.674 grams of gypsum for each 100 cubic centimeters.

LIMESTONE AND CALCAREOUS MATERIALS.

1. These should be fine grained and uniform in composition and structure.

2. The magnesia should be low enough so that in the cement a content of 3 per cent. of magnesia is not exceeded.

3. The alumina content should not be high enough to disturb the proper silica-alumina ratio in the cement.

4. The content of ferric oxide must not be so high as to increase the amount of ferric oxide in the cement beyond 4 per cent.

5. It should be low in sulphur and free from concretionary iron sulphide.

In the consideration of calcareous materials, the most important question is that of the magnesia content, as the restricting clause in regard to the magnesia rules out many otherwise excellent materials. In many cases the limit of magnesia is exceeded but slightly and it seems a pity that such materials should be rejected. The fact is that it is unjust to throw out a material on account of one or two per cent. of magnesia in excess over the three per cent., as many tests have shown that a magnesia content even up to 7 per cent. in an otherwise well proportioned cement has no deleterious influence. It might be well to cite some investigations covering this point. Dyckerhoff's elaborate experiments, it is true, condemned magnesia. His work included the duplicate testing of various contents, both in regard to the tensile strength for periods up to five years, and the measurement of the increase in volume in terms of the linear expansion of a bar of cement 100 mm. long, made by careful micrometer measurements. The results obtained by him are summarized in the curves on pages 227-9.

Meyer, on the other hand, denies most emphatically that magnesia is a dangerous constituent. Blaese allows as much as 10 per cent. of magnesia. Tetmayer reports two vitrified cements of the analysis shown in table on page 230, as having stood the tests for constancy of volume.

The tensile and crushing strength expressed in kilograms per sq. cm. were found by him as given in the second table on page 230.

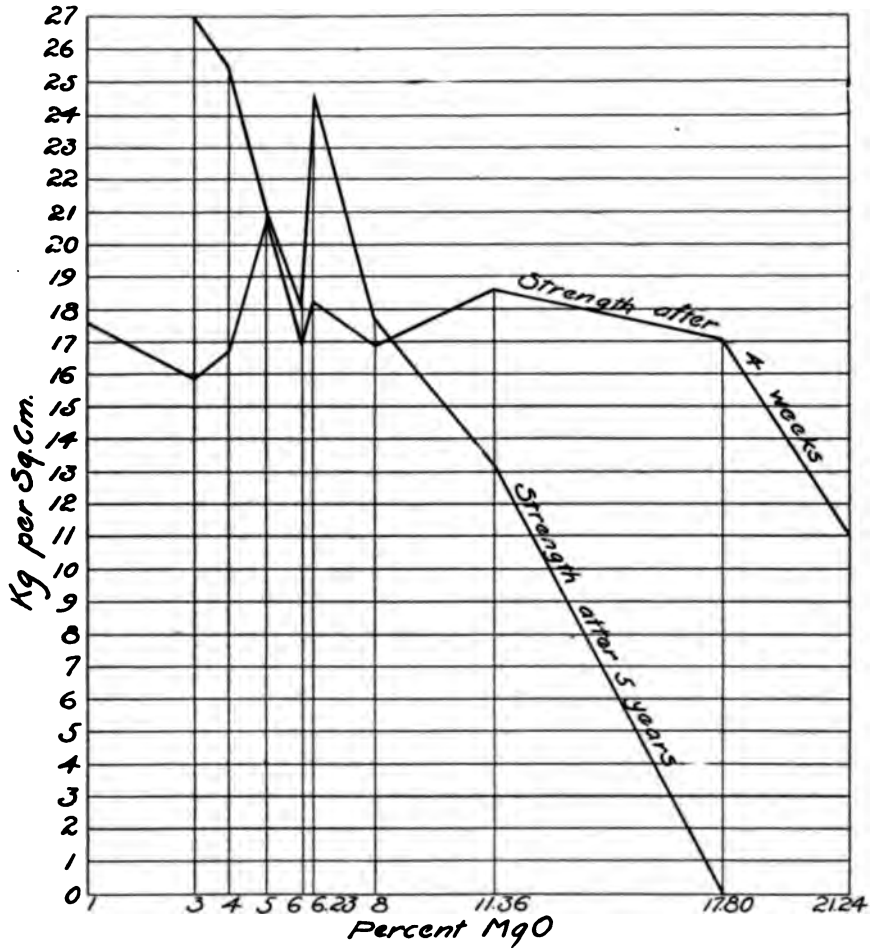

Fig. 25. Dyckerhoff's experiments on magnesia, showing tensile strength of high magnesia cements deteriorating with age.

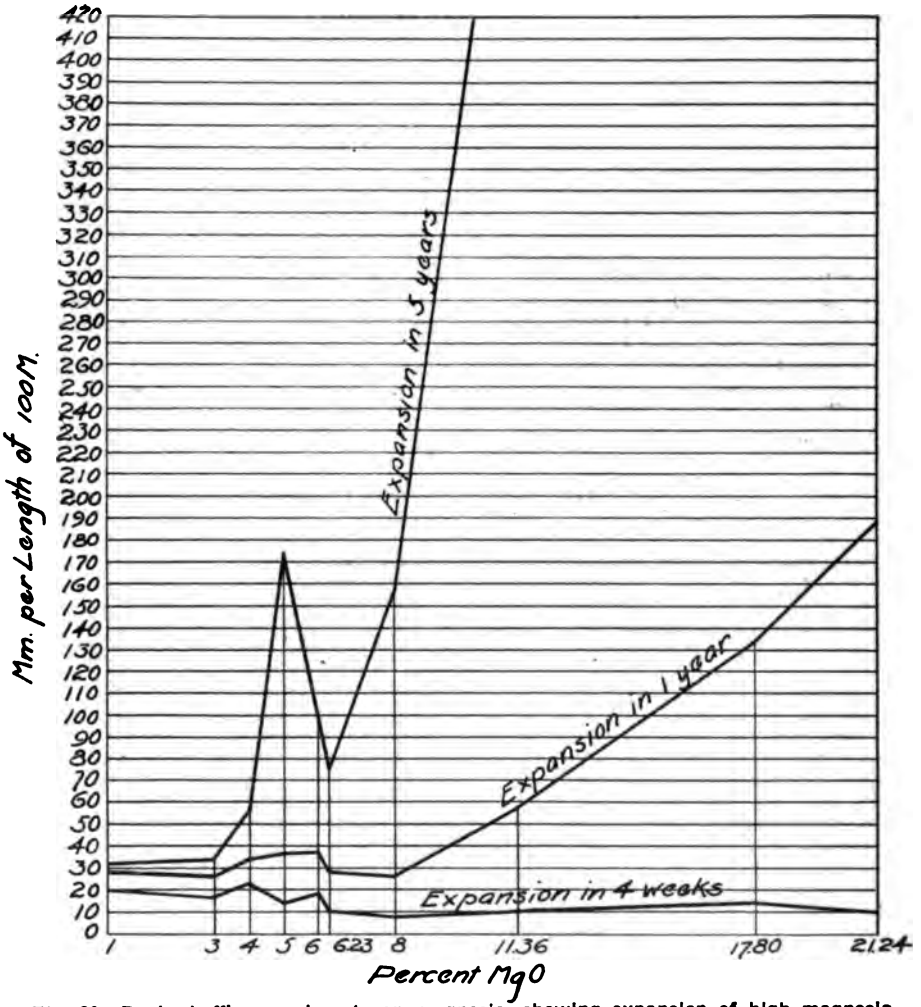

Fig. 26. Dyckerhoff's experiments cn magnesia, showing expansion of high magnesia cements increasing with age.

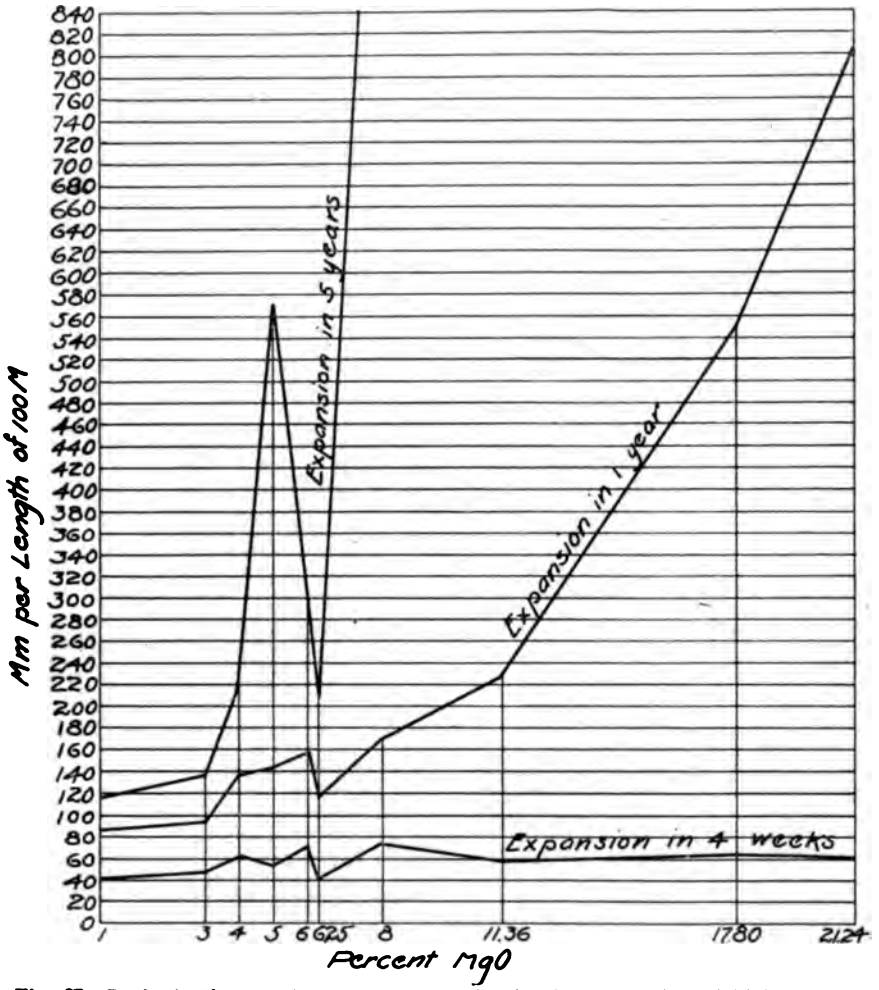

Fig. 27. Dyckerhoff's experiments on magnesia showing expansion of high magsesia cements increasing with age.

Composition of Two Vitrified Cements, by Tetmayer.

	Per Cents.	
	A.	B.
Silica	17.06	19.92
Alumina	5.28	7.01
Ferric oxide	3.07	2.73
Lime	48.45	35.29
Magnesia	17.28	8.39
Calcium sulphate	1.85	2.43
Loss on ignition	6.36	4.57

Tensile and Crushing Tests of Two Vitrified Cements, by Tetmayer.

Number.	Kind of test.	28 days.	1 year.	2 years.	3 years.	4 years.	5 years.	6 years.	8 years.	10 years.
A.	Tensile strength	20.1	45.6	39.0	39.1	43.7	38.8	41.0	44.1	43.4
	Crushing strength	118.9	231.6	293.8	406.2	393.8	379.0	455.6	421.0	413.8
B.	Tensile strength	33.5	57.9	57.3	60.5	68.0	60.3	60.4	64.8	63.5
	Crushing strength	207.6	363.8	.....	.....	372.8	.....	581.6	.....	614.7

In 1893 Kawalewsky made an extensive report on vitrified magnesia cements which after ten years were still found to be in excellent condition and showing great strength.

Golinelli in 1895 reported a carefully arranged series of tests with magnesium Portland cements containing an average of 26 per cent. of magnesium oxide and corresponding to the ratio

$$\frac{CaO+MgO}{SiO_2+Al_2O_3+Fe_2O_3}=2.06.$$

The silica-alumina ratio maintained was 3. These cements possessed most excellent strength and were entirely constant in volume. This investigator came to the conclusion that magnesia may be substituted for lime. On the other hand, it cannot be denied that some high magnesia cements have given trouble in practice, as a number of well authenticated cases are on record. This, together with the consideration

of the character of magnesia, its slow hydration, must lead to the general conclusion that dolomitic Portland cements are found to show two distinct rates of hydration, one due to the hydration of the lime compounds, the other due to the magnesium reactions.

Magnesia is active only at lower temperatures, and its rate of hydration is the slower the higher the compound has been burnt. But since two hydrations, a rapid and a slow one, cannot take place in a cement without injuring the structure, we must conclude that the cement should not contain enough magnesia to exert any appreciable influence. However, a content of magnesia up to 5 per cent., according to the experiments made so far, has proven harmless.

CALCULATION OF PORTLAND CEMENT MIXTURES.

For the calculation of the necessary amounts of clay and lime carrying material we have several available methods which we shall discuss briefly.

The Chatelier Formula.—American cement chemists make extensive use of the limiting Chatelier formula modified by Newberry:

$$x(3CaO+SiO_2)+y(2CaO+Al_2O_3).$$

Let us assume we have a clay of the formula:

$$Al_2O_35SiO_20.22Fe_2O_32H_2O$$

and, say, a pure limestone. We would have then the formula:

$$3xCaO+xSiO_2+2yCaO+yAl_2O_3, \text{ or}$$
$$(3x+2y)CaO+xSiO_2+yAl_2O_3.$$

But the clay contains 5 molecules of silica and 1 of alumina and the required molecules of calcium oxide will be:

$$(15+2)=17CaO.$$

We find, hence, that the values x and y are the co-efficients of the molecules of silica and alumina in the clay. The formula of the cement is then:

$$17CaO5SiO_2Al_2O_30.22Fe_2O_3.$$

The sum of the molecular weights of the clay formula is:

$$5SiO_2+Al_2O_3+0.22Fe_2O_3+2H_2O=473.2.$$

Therefore the limestone and the clay must be mixed in the ratio of 17×100 (molec. weight of calcium carbonate)$=1700:473.2$, or for each part by weight of the clay $1700\div473.2=3.59$ parts of limestone must be taken.

We can, however, attack the problem from another standpoint, making use not of the formula, but of the percentage composition of the clay, which according to the above formula would be:

	Per cents.
Silica	63.40
Alumina	21.55
Ferric oxide	7.44
Chemical water	7.61

The limiting formula $x(3CaOSiO_2)+y(2CaOAl_2O_3)$ can at once be translated into terms of parts by weight; since 3 molecules of calcium oxide are required for one of silica, we can say that $3\times56=168$ parts by weight of lime are needed for $1\times60=60$ parts of silica, or for one part of silica 2.8 parts of calcium oxide are required. In terms of the carbonate $(3\times100)\div60=5$ parts are needed for one part of silica. Likewise we find that one molecule of alumina requires 2 molecules of lime, and hence one part of alumina must have 1.1 part of lime, or $200\div102$=nearly two parts of carbonate. The calculation now becomes very simple:

63.40 parts of silica demand $63.4\times5=317.09$ parts of carbonate.
21.55 parts of alumina demand $21.55\times2=$ 43.19 parts of carbonate.

360.28

100 parts of clay demand hence 360.28 parts of carbonate or 1 part must have 3.6 parts of the limestone, which is practically the same as the ratio obtained in the first problem.

The Limitations of the Chatelier Formula.—The Chatelier formula does not give entire satisfaction, however. For instance, taking the formula

$$17CaO,\ 5SiO_2,\ Al_2O_3,\ 0.22Fe_2O_3$$

we find the percentage composition to be:

	Per cents.
Lime	68.54
Silica	21.60
Alumina	7.34
Ferric oxide	2.53

It will be noticed that the content of lime is higher than that of the average Portland cement. We assumed, however, that no fluxes were present; in using a clay with other fluxes like potash and soda the percentage of the calcium oxide would be reduced somewhat. This is due to the fact that the formula used is an ideal one, which requires ideal conditions of blending, that is, perfect pulverization which cannot be obtained in practice. However, it might be perfectly feasible to produce a

cement of this composition in the rotary kiln. The writer had no difficulty in burning such a cement without resorting to high temperature test furnaces. There is, however, some difficulty in keeping this up continually, since the high temperature would make the burning more expensive, the kiln linings subject to greater deterioration, and would increase the practical difficulties in operating the kiln. In addition, owing to the invariable fluctuations in the fineness of grinding, this high lime content would make longer storing necessary, which would likewise raise the cost. It might yet be mentioned that the above cement vitrifies thoroughly at about 1400° C.

Things become more serious, however, when we use a clay with a higher content of silica, say with the formula $Al_2O_3 6.66SiO_2 0.30Fe_2O_3 2H_2O$, which is by no means unusual or arbitrary. In fact, there are many clays which show a much higher molecular proportion of silica. Since we know the lime content of the cement to be a function of x, the number of the silica molecules in the clay, it is bound to rise with the silica content of the clay. This clay, hence, would make a cement of the following composition:

	Per cents.
Lime	69.83
Silica	21.95
Alumina	5.60
Ferric oxide	2.63

The sum of the lime and silica percentages is hence 91.78, which indicates that the fusible magma whose function it is to start the vitrification is very small in amount, not sufficient to bring about vitrification at temperatures within practical reach. This is, of course, shown still more strikingly by more silicious clays, so that no amount of fine grinding could produce a good cement at the temperatures practically obtainable. The formula

$$x(3CaO+SiO_2)+y(2CaO+Al_2O_3).$$

is therefore inherently wrong when applied indiscriminately in practical work, and must be corrected either by a change in the molecular proportions or by the use of a constant for the various degrees of acidity of the clays.

Experiments on the Use of Different Formulae.—In order to study the effect of the use of different formulas in the dry preparation of Portland cements, the writer made up synthetic mixtures of kaolin, fine ground quartz, calcium carbonate and ferric oxide in quantities of about 20 pounds of raw mixture, grinding the materials together in an iron ball-mill for five hours. The iron oxide content was intended to be kept at about 3 per cent. These cements were then made up in five series of the following formulæ: $(3CaO)SiO_2$, $(2CaO)Al_2O_3$; $(2.9CaO)$

SiO_2, $(2CaO)Al_2O_3$; $(2.8CaO)SiO_2(2CaO)Al_2O_3$; $(2.7CaO)SiO_2(2CaO)Al_2O_3$; $(2.6CaO)SiO_2$, $(2CaO)Al_2O_3$.

Each series again was made up of five members, in which the ratio of clay substance to free silica, which is also expressed by the silica-alumina ratio, was made to vary. The following ratios were employed: 1.2, 1.9, 2.4, 3.1, 4.1.

The compositions of these cements are tabulated as follows:

Number.	Calcium oxide per cent.	Silica per cent.	Alumina per cent.	Ferric oxide per cent.	Magnesium oxide per cent.	Ratio, SiO_2, Al_2O_3, by per cents.	Ratio, SiO_2, Al_2O_3, by molecules.	Formula.
1	64.15	17.27	14.25	3.09	1.30	1.21	2.20	$(3CaO)SiO_2(2CaO)Al_2O_3$
2	65.93	19.55	10.30	2.87	1.34	1.90	3.22	
3	66.23	20.82	8.64	2.93	1.35	2.41	4.24	
4	66.98	21.68	7.04	2.95	1.36	3.08	5.23	
5	68.16	22.23	5.40	2.86	1.39	4.12	7.00	
6	63.83	17.68	14.47	2.69	1.30	1.22	2.07	$(2.9CaO)SiO_2(2CaO)Al_2O_3$
7	65.73	19.88	10.28	2.83	1.34	1.93	3.28	
8	66.19	20.87	8.62	2.88	1.35	2.42	4.11	
9	66.73	21.86	7.07	2.93	1.36	3.09	5.25	
10	67.54	22.64	5.71	2.74	1.37	3.97	6.74	
11	62.38	17.50	14.99	2.82	1.27	1.17	2.00	$(2.8CaO)SiO_2(2CaO)Al_2O_3$
12	64.72	20.42	10.72	2.81	1.32	1.90	3.20	
13	65.50	21.27	8.85	2.82	1.33	2.40	4.08	
14	66.35	22.33	7.11	2.84	1.35	3.14	5.33	
15	67.31	22.76	5.59	2.77	1.37	4.07	6.92	
16	....	....	....	....	....	....	....	
17	64.35	20.61	10.82	2.86	1.31	1.91	3.24	$(2.7CaO)SiO_2(2CaO)Al_2O_3$
18	64.99	21.80	9.01	2.88	1.32	2.42	4.11	
19	65.76	22.70	7.32	2.89	1.34	3.10	5.26	
20	66.30	23.76	5.65	2.96	1.35	4.20	7.14	

The high-lime mixtures were burnt in a crucible furnace, lined with magnesite, fired with gasoline gas; the low-lime cements were burnt in an up-draft test kiln. All of the cements were cooled rapidly in the air as soon as vitrified. Owing to the iron content it was an easy matter to determine when vitrification had set in. No

difficulty was experienced in reaching the required temperatures, which ranged from 1270 to 1400° C. as measured by the Chatelier pyrometer. The burning temperature of the cements 1 to 5 was not determined, since the thermo couple could not be inserted in the crucible furnace without some risk to the wire. The clinker was carefully sorted, all underburnt as well as fused pieces being rejected. Owing to fear of contamination, the cements were ground in a mortar by hand and put through a 100 mesh sieve. The cement after screening, however, was found to be rather lacking in really fine dust, and hence did not show up as well in the tensile tests as cement ground in a ball-mill would.

The results of the tests are compiled in the following table:

Number.	Formula.	Ratio $\frac{SiO_2}{Al_2O_3}$.	Appearance of clinker.	Tensile strength 1:3, pounds per sq. in. 28 days.	Boiling test.
1	$(3CaO)SiO_2\ (2CaO)Al_2O_3$.....	1.21	Yellowish, fusible.	49	Poor
2	"	1.90	Slightly yellow.	187	Poor
3	"	2.41	Good clinker.	180	Fair
4	"	3.08	Good clinker.	187	Fair
5	"	4.12	Good clinker.	203	Poor
6	$(2.9CaO)SiO_2\ (2CaO)Al_2O_3$	1.22	Brown slag.	.....	Poor
7	"	1.93	Fairly good.	193	Poor
8	"	2.42	Good.	168	Fair
9	"	3.09	Good.	232	Good
10	"	3.97	Good.	230	Good
11	$(2.8CaO)SiO_2\ (2CaO)Al_2O_3$.....	1.17	Slag like.	109	Poor
12	"	1.90	Fairly good.	228	Poor
13	"	2.40	Good.	305	Good
14	"	3.14	Good.	221	Good
15	"	3.97	Good.	188	Good
16					
17	$(2.7CaO)SiO_2\ (2CaO)Al_2O_3$.....	1.91	Fairly good.	102	Poor
18	"	2.42	Good.	67	Poor
19	"	3.10	Good.	122	Good
20	"	4.20	Good.	225	Good

The cements were allowed to cure for four weeks, but no gypsum was added. This, of course, made the high alumina cements quite quick setting. Five briquettes were made of each cement, 1 cement: 3 standard sand. Two boiling tests, 6 hours' boiling, were also made of each cement. Beginning with the formula $(2.6CaO)SiO_2(2CaO)Al_2O_3$, dusting was observed, and very low and unsatisfactory tests were obtained both as regards tensile strength and boiling tests. For this reason these have been omitted from the table.

In considering the results of the tests it must be remembered that cements with a silicious clay base harden much more slowly than aluminous cements, but attain after six months very high strengths, though showing up less promisingly in the short time tests. This was found to be true in a number of other experiments.

Conclusions.—1. From these results we can make the assertion that for dry ground mixtures the formula $(2.8CaO)SiO_2$, $(2CaO)Al_2O_3$ is the safest. This would correspond to the proportion, in parts by weight, of 1 part of silica to 2.61 parts of lime, or 1 part of silica to 4.66 parts of calcium carbonate. A cement made from a silicious clay and limestone would be decidedly unsafe with the theoretical tri-calcium silicate formula. From the results, however, no deductions can be drawn with reference to the theoretical silicates present in the cement. But the work seems to support the views of Vogt that we are dealing with a slag whose limits of composition are not as narrow as we might suppose. But at the same time there are quite definite limits, for with a formula of $(2.6CaO)SiO_2$, $(2CaO)Al_2O_3$, hydraulicity, as we know it in Portland cements, practically ceased and "dusting" began. This means that at this point hydraulic silicates can not crystallize out any longer. No coal ash was added to these cements at all, since they were not in contact with coal. The objection might be made that the formula would give too low a lime content owing to the introduction of silica and alumina in the ash from the coal when burnt in the rotary kiln. There is some justice in this objection, as the tendency of the ash will be to lower the lime content, and undoubtedly some reaction takes place.

Yet this naturally depends on the amount and composition of the ash and cannot be allowed for offhand, but must be regulated for each individual case. But the effect of the ash according to testimony collected from cement chemists is much less than is frequently supposed. That the cement composition is distorted by the presence of ash is, of course, obvious, and hence the usual analysis of a cement does not show its true composition. This can only be obtained by the ignition of the raw mixture without contact with coal. The fixing of the above practical formula does not take away the value of the Chatelier-Newberry formula as a limiting formula.

2. The ratios of silica to alumina given on several occasions seem to be correct, for the safest cements in the boiling test, though not the highest in the tensile test, are those with a silica-alumina ratio of from 3:1 to 4:1. Aluminous cements are to be condemned.

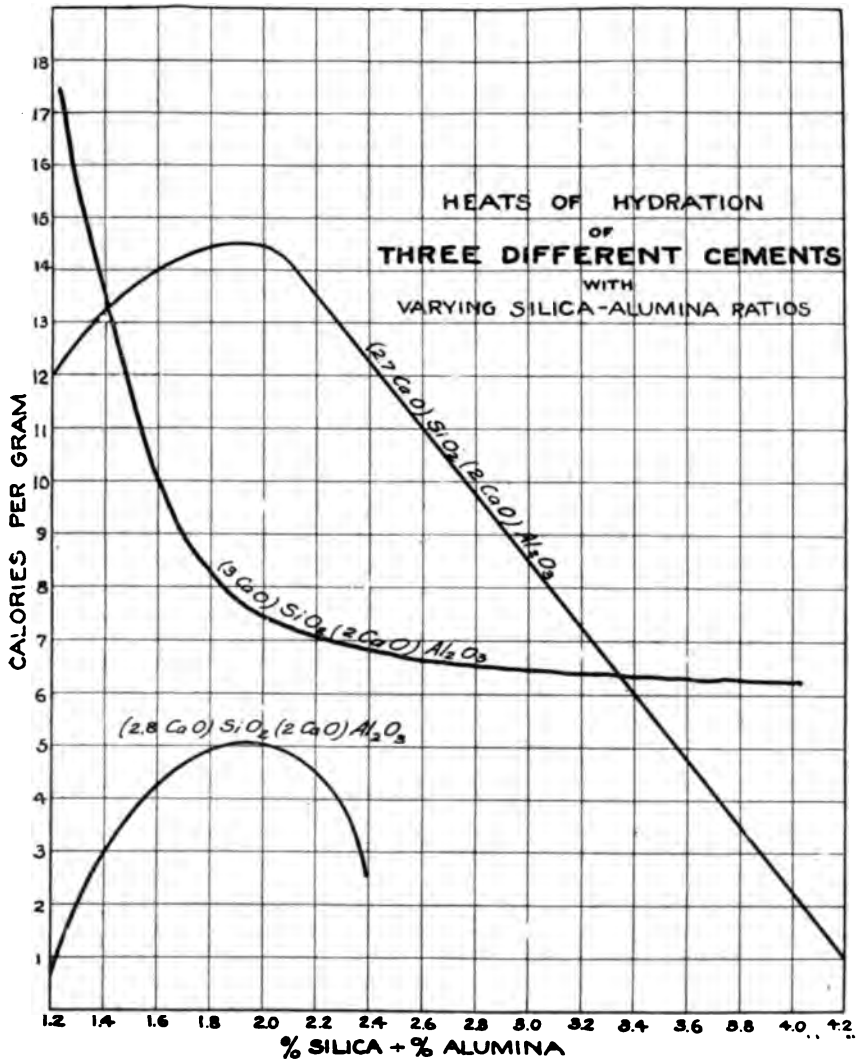
HEATS OF HYDRATION
OF
THREE DIFFERENT CEMENTS
WITH
VARYING SILICA-ALUMINA RATIOS
(2.7 CaO) SiO2 (2 CaO) Al2O3
(3 CaO) SiO2 (2 CaO) Al2O3
(2.8 CaO) SiO2 (2 CaO) Al2O3
CALORIES PER GRAM
% SILICA + % ALUMINA
1.2 1.4 1.6 1.8 2.0 2.2 2.4 2.6 2.8 3.0 3.2 3.4 3.6 3.8 4.0 4.2
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18

Fig. 28. Curves showing heats of hydration of three cements of varying silica-alumina ratios.

Some of these cements were tested in the calorimeter by Mr. Edward Thomas, a former student of the writer. Ten grams of the cements were taken and 100 cc. of distilled water. The results of these determinations are plotted in the accompanying curve, and show quite clearly that the silicious cements possess lower heats of hydration in spite

of a higher lime content than the more aluminous clay bases. Unfortunately these tests are not quite as complete as it was desired to have them. It was also intended to carry on these tests by adding to the cements a little more water than they require for complete hydration, say 25 per cent., placing the cement and water into a metal capsule and immersing the latter in water. The rise in temperature would then give the hydration value under conditions approaching the practical reaction. Time, however, did not permit of carrying out these tests. For purposes of comparison the hydration values of a number of standard Portland cements are given, using 10 grams of the sample and 100 cc. of water.

	Calories per Gram.
No. 1	3.43
2	6.41
3	1.35
4	3.98
5	1.04

In order to supplement the results of the preceding series in regard to the best practical formula for dry ground mixtures of clay and limestone, the following cements were prepared, using as a basis a silicious clay found on the campus of the Ohio State University, a drift deposit of the following composition:

	Per cents.
Silica	68.82
Alumina and iron oxide	19.20
Calcium oxide	2.69
Magnesium oxide	2.46

The limestone was a Carboniferous stone from near Wellston, Ohio, of the composition:

	Per cents.
Calcium carbonate	91.80
Silica	3.52
Alumina and iron oxide	3.51

These materials were mixed and ground together intimately in the dry condition in an iron ball-mill, containing flint pebbles. The time of grinding was four hours, and practically no residue was left on the 100 mesh sieve.

The clinker, after burning to complete vitrification, was ground in the ball-mill to a powder, leaving no residue on the 100 mesh sieve. No gypsum was added to the cement. The results of the test were as follows:

Formula employed.	Tensile strength 1:3, 28 days. Pounds per sq. in.	Boiling test.
$(2.9CaO)SiO_2\ (2CaO)Al_2O_3$.....	290	Good.
$(2.8CaO)SiO_2\ (2CaO)Al_2O_3$.....	360	Good.
$(2.7CaO)SiO_2\ (2CaO)Al_2O_3$.....	225	Good, off glass

Five briquettes were used in each test. This work was repeated with practically the same results by two students.

Examples of Cement Batch Calculation.—To illustrate the method of calculating the composition of a cement mixture, the following example is worked out:

Given the clay mentioned above:

68.82 % silica,
19.20 % alumina and iron,
2.69 % calcium oxide,
2.46 % magnesium oxide.

and the limestone:

91.80 % calcium carbonate,
3.52 % silica,
3.51 % alumina and iron.

The formula $(2.8CaO)SiO_2$, $(2CaO)Al_2O_3$ requires for every part by weight of silica 4.66 parts of calcium carbonate, and for every part of alumina two parts of the carbonate. The clay requires, therefore,

$68.82\times4.66=320.7$ parts,
$19.20\times2.00=\ 38.4$ parts.

359.1 parts calcium carbonate.

But as the clay contains 2.69 per cent. calcium oxide, we must deduct this amount, as the carbonate, and we obtain: $359.1-(2.69\times(100\div56)=354.3$ parts of calcium carbonate required.

On the other hand, the limestone contains silica and alumina, which take up some of the calcium present, so that the amount available is $91.8-(3.52\times4.66+3.5\times2)=68.4\%$ of calcium carbonate. The amount of limestone to be used for one part of the clay is therefore $354.3\div68.4=5.179$ parts, or 100 parts of clay require 518 parts of limestone. In this calculation the ferric oxide has been taken together with the alumina, as the difference due to allowing for the iron is negligible. In practical work the calculation is simplified by the use of logarithms, curves, or tables analogous to the slag tables used in blast furnace work.

Meyer's Method.—There are also other methods of calculating cement mixtures. Meyer thus advises the use of the formula:

$$x((3CaO)SiO_2)+y((nCaO)SiO_2R_2O_3),$$

in which the value of n=3 to 4. This is highly commended by some European chemists. This formula has also been stated as follows: $aMO+bAl_2O_3+1SiO_2$, in which MO is the sum of the equivalents of lime, magnesia, iron oxide and alkalies, *a* is equal to the minimum value, 3, and the maximum value 3+b, *b* of course is the equivalent of alumina. Illustrating the application of this formula by an example* and assuming that we are dealing with two materials of the following composition:

	Limestone.	Marl clay.
Silica	1.2	42.0
Alumina	0.5	10.2
Calcium oxide	50.4	22.4
Magnesia	1.6	....
Ferric oxide	....	4.0
Loss on ignition	46.3	21.4

we obtain the equivalents by dividing each percentage by its molecular weight.

If now x is the number of parts by weight for one part of clay, the mixture, raw or burnt, contains:

Lime plus fluxes (=MO)	$0.94x+0.95$
Alumina	$0.005x+0.10$
Silica	$0.02x+0.70$

For a cement of the lower lime limit ($CaO=3SiO_2$) we have

$$0.94x+0.45=3(0.02x+0.70).$$

For the upper lime limit ($CaO=Al_2O_3+3SiO_2$) we obtain:

$$0.94x+0.45=0.005x+0.10+0.02x+0.70.$$

For a medium limit we have:

$$0.94x+0.45=\tfrac{1}{2}(0.005x+0.10)+3(0.02x+0.70).$$

Solving for x, we find it equal to 1.94. Hence for one part of clay there must be used 1.94 parts of limestone. The cement contains, then:

$$2.27MO+0.1097Al_2O_3+0.7388SiO_2.$$

Letting $SiO_2=1$, the formula will be:

$$3.075MO+0.15Al_2O_3+1SiO_2,$$

which is the desired composition.

*Taken from the *Tonindustrie Zeitung*.

Hydraulic Modulus Method. —A method of calculation generally used in Europe depends on the so-called hydraulic modulus, which may be stated as follows:

$$\frac{\text{Per cent. calcium oxide}}{\text{Per cent. silica+per cent. alumina+per cent. ferric oxide}}=2.$$

That is, the content of calcium oxide should be twice as great as the sum of the percentages of silica, alumina and ferric oxide. The permissible variations range from 1.8 to 2.2. This formula is much cruder and more inaccurate than the Chatelier formula, as it does not discriminate between the three constituents in the denominator, for the requirements of the formula would be met just as well by a highly aluminous clay or a silicious iron ore. However, it gives a readily available check on the other method, provided a suitable clay is being used. The sum of the three constituents, silica, alumina and iron is briefly called "silicate"$=s$. The lime contents we let$=c$ and the modulus n. If a clay contains s parts of silicate, and c parts calcium oxide, the latter requires $c\div n$ parts of silicate, which is to be subtracted from the s parts of silicate. The remaining parts of silicate, $s-(c\div n)$, require n times as much lime, or $n[s-(c\div n)]$ parts of calcium oxide.

If the limestone contains s_1 parts of silicate and c_1 parts of lime, the former requires again $n.s_1$ parts of the latter, so that there are available only $c_1-n.s_1$ parts of calcium oxide. We know, however, that the clay requires $n[s-(c\div n)]$ parts of lime,and hence as many parts of limestone must be taken as will furnish the required number of parts of caustic lime or the ratio must be:

$$n\left(s-\frac{c}{n}\right)\div(c_1-n.s_1)$$

This gives the formula:

$$\frac{\text{Limestone}}{\text{Clay}}=\frac{n\left(s-\frac{c}{n}\right)}{c_1-n.s_1}=\frac{n.s-c}{c_1-n.s_1}$$

To illustrate:* A clay contains 63 per cent. of silicate and 25 per cent. of calcium carbonate$=14$ parts of calcium oxide. The limestone contains 10 per cent silicate and 87.5 per cent of carbonate$=49$ parts of caustic lime. If the modulus is to be 2, the proportion of limestone and clay to be used is:

$$\frac{\text{Limestone}}{\text{Clay}}=\frac{2\times(63-14)}{49-(2\times10)}=\frac{112}{29}=\frac{3.86}{1}$$

This method of calculation is not recommended for general use.

*Schoch, *Moertelmaterialien*, p. 90.

A Simple Algebraic Method.—After once the best proportion of a mixture has been established, the daily mixture can be calculated from the raw materials available by a simple calculation depending on the lime content of the two materials.

Let x=weight of limestone in charge,
y=weight of clay in charge,
a=per cent. of calcium oxide in the limestone,
b=per cent. of calcium oxide in the clay,
c=per cent. of calcium oxide in the mixture,

then $c=\frac{ax+by}{x+y}$ or $x(a-c)=y(c-b)$ or $\frac{x}{y}=\frac{c-b}{a-c}$

Experimental Apparatus for Cement Burning. —Preliminary burning tests are made by weighing out the ingredients, grinding them to a powder in a ball-mill, moistening the dust and making into small balls or cubes and burning them in a test kiln. The writer employed for grinding his mixture the iron ball-mill already mentioned, which has the shape of a flattened sphere, 24 inches in diameter and 7⅞ inches wide at the center, making 27 revolutions per minute. The mill is made of chilled iron, and provided with a cap whose surface, as well as the surface of the mill opening, are ground, forming a tight joint. With 126 pounds of flint pebbles, 30 to 40 pounds of mixture can be ground sufficiently fine in from three to five hours. This mill is shown in Fig 29.

For the burning the writer employed a crucible furnace, lined with a mixture of 90 parts of burnt magnesite and 10 parts of Portland cement, with an inside diameter of 4 inches and a height of 6 inches, fired with gasoline gas, and using air under a pressure of about 18 pounds to the square inch, furnished by a Westinghouse locomotive air pump. This was quite satisfactory for smaller quantities; after once heated, a highly calcareous cement could be burnt in 20 minutes. The furnace space was simply filled with the balls of the raw mixture which were, of course, perfectly dry.

For larger quantities of cement requiring a high temperature a furnace shown by figure 30 on page 245 was used which consisted essentially of a straight shaft of fire-brick, with 4 inch walls, and divided into three distinct divisions. Into a space 4 inches high at the bottom, air was forced under a pressure of about 12 ounces, from a blower through a 2 inch pipe. This space was divided from the next division by means of a cast iron plate provided with concentric rows of holes. Above this plate, about 5 inches away from it, an iron pan was

supported by two bricks, petroleum being fed into this pan by means of a ¼ inch pipe. The oil was forced in by gravity from a can some distance away from the furnace. On this pan evaporation of the petroleum took place after the furnace was in operation. Several inches above the pan, the whole cross-section of the shaft was filled with broken firebrick so as to bring about the mixture of the petroleum vapors with the air blown in.

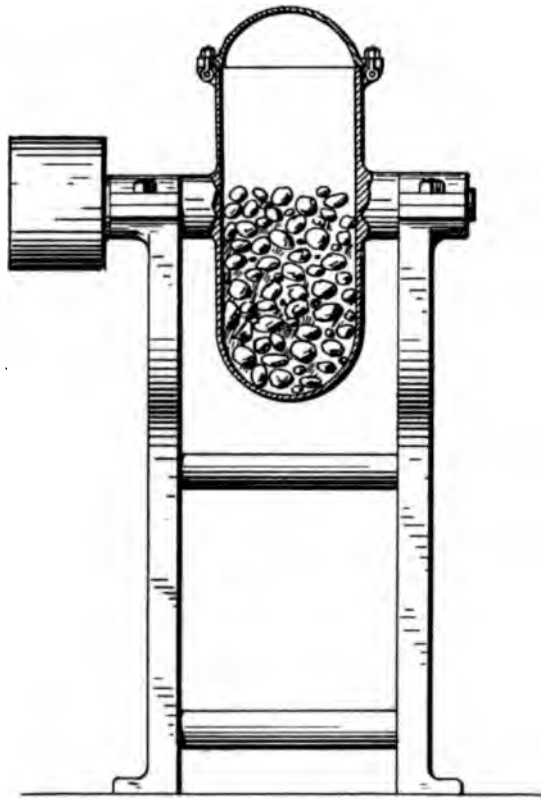

Fig. 29. Ball mill for grinding samples of cement.

Above this compartment the third compartment was formed by a grating of bricks. At first magnesite bricks were used, later porous bricks from a mixture of 80 per cent. magnesite and 20 per cent. of Portland cement were employed. On this grating the balls of cement mixture were heaped up to the top of the compartment which had a height of 8 inches. The cover consisted of a perforated clay tile upon which were piled broken bricks, so as to keep the heat from rushing out too rapidly. The clinker compartment was accessible from the outside by means of a door, which was closed by a firebrick plug which could be removed and the clinkers withdrawn and examined.

This furnace can be readily used for high temperatures. The time required to make a burn, including the heating up, is about two hours, A hole at the level of the iron plate permits of introducing the small amount of paper and wood necessary to start the flame, by heating the pan. By removing the pan, bricks and broken pieces, this furnace was also used for burning with coke, which, though not as convenient and rapid, was accomplished successfully. An opening, closed by a plug, beneath the plate, permitted of withdrawing the fine dust and ashes which filtered through, while the coal clinkers were removed through the hole at the level of the plate. The coke was charged through a door just beneath the grating supporting the cement clinker. In firing with coke, it was found best to use a good grade of firebrick, since the magnesite bricks, even those made of the magnesite-cement mixture, proved to be too brittle and friable to withstand the sudden cooling on opening the door. The layer of coke must be kept as thick as possible.

An updraft kiln of the Ohio State University Ceramic Department was also used successfully for burning ordinary cement mixtures, a temperature of cone 12, 1370° C. being attained without difficulty. For the usual testing work where contamination with the ash of the fuel is not objectionable, the ordinary type of the shaft furnace, similar to an assay furnace, without a muffle, the draft being furnished by a stack, is quite sufficient. It is simply a rectangular shaft, with a grate and ash-pit bottom. Wood is placed on the grate and on top of that a heavy layer of coke. Cubes of cement mixture are charged on top of the fuel in a thin layer, followed by more coke. In this manner alternate layers of coke and cement are arranged.

Professor Campbell, of the University of Michigan, used, very successfully, a small rotary kiln, consisting of an inclined iron pipe, 8 inches in diameter and 32 inches long, which was lined with four sections of a hard burnt magnesite pipe, whose inside diameter is 3 inches. The furnace is rotated by means of a ½ horsepower motor and makes one revolution in 1 minute and 25 seconds. It is fired by means of a Hoskins gasoline burner and air is supplied at about 50 pounds to the square inch. On measuring the temperature by means of the Chatelier pyrometer, it was found to be the highest about 6 inches from the lower end, it being 1500° C. After the kiln is heated up, the mixture is charged and with an inclination of 6° takes 25 to 35 minutes to pass through the kiln. During the first hour 1,500 to 1,700 grams are fed; after the first hour, 1,000 to 1,200 grams per hour; this means 600 to 700 grams of clinkered material per hour.

For research work, electrical furnaces are extremely useful, allowing of quick firings and absolute control of the temperature. Platinum foil

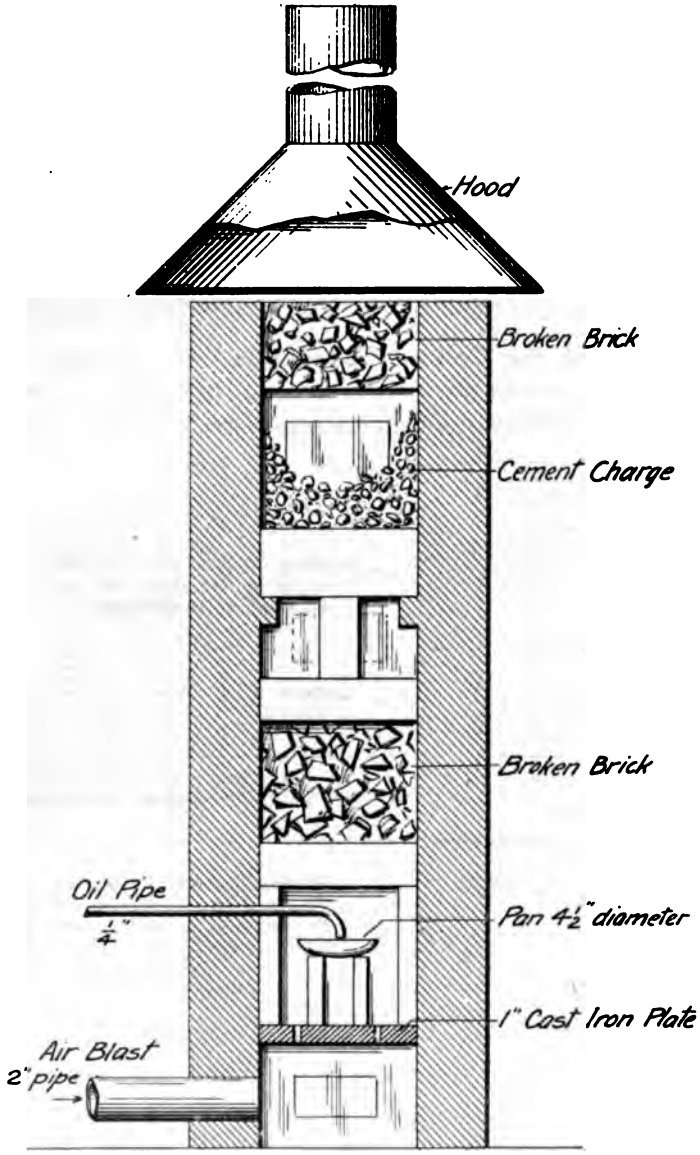

Fig. 30. Kiln for burning sample batches of cement.

resistance furnaces, however, are quite troublesome above a temperature of 1200° C., owing to the conduction of the heating cylinder and consequent danger of short circuits. The Hempel carbon resistance furnace would prove very suitable, and of late a furnace has been offered on the market which certainly seems to be an exceedingly simple apparatus, consisting mainly of a refractory cylinder of fire-clay or basic material surrounded by a special resisting material, called "Kryptol." It is claimed that the "Kryptol" furnace produces a temperature of 2000° C. quite readily, depending on the refractoriness of the cylinder. It consumes from 3 to 5 kilowatts per hour, according to the temperature and size. The temperature measurements must be made with an optical pyrometer, but can be carried out even with an ordinary photometer.

Corrections of the Cement Composition.—In the following table a few general corrections are given which may be followed if the clinker produced, experimentally or on a large scale, shows certain defects:

Defect of cement.	Correction.
Too difficult to vitrify.	Decrease lime content, or add more ferric oxide in the shape of an ore, or add fluorspar to raw cement.
Vitrified too rapidly.	Increase silica content of clay base and lime content.
Yellowish clinker.	Increase silica content in clay base.
Sets too rapidly.	Increase silica content in clay base, or add fluorspar to raw mix, or add ferric oxide to raw mix, or add ground gypsum to burnt cement.
Sets too slowly.	Reduce silica content.
Not constant in volume (does not stand boiling test.)	Store longer. Decrease lime content or increase content of ferric oxide, or increase silica content in clay base; grind raw mixture finer; reduce sulphur content.
Tendency to dust.	Increase lime content; quench clinker in water or cool rapidly in air; add ferric oxide to raw mix.

Defect of cement.	Correction.
Too low in initial tensile strength.	Increase lime content and grind raw mix finer, or increase alumina somewhat; grind clinker finer.
Too low in final tensile strength or showing a deterioration in strength.	Increase silica in clay base.

CHAPTER VII.

WINNING AND PREPARATION OF THE RAW MATERIALS.

According to the nature of the various raw materials the method of winning them must differ. It is impossible to consider all the details of the quarrying and digging, but we must let it suffice to make a brief outline of the processes practicable.

THE CLAYS.

As to the clays, we have, according to their nature, the following methods of winning them:

1. Hand digging.
2. Quarrying.
3. Use of plow and scraper.
4. Steam shovel.
5. Dredging.
6. Mining.

Hand Digging.—Hand digging is practiced where the daily output is small and the clay is soft enough to be picked and shoveled without too much effort. The cost of digging clay is at least 35 cents per cubic yard.

Quarrying.—Quarrying is employed with shales. The material is worked in benches and is blasted with powder, dynamite being as a rule too quick in its action. By means of proper "undercutting" large quantities of material can be handled. The cost is probably around 25 cents per cubic yard.

Plow and Scraper.—The plow and scraper are very suitable in larger areas of soft clay, comparatively level. The common scrapers should not be used for distances over 200 feet. For greater distances a platform may be used, to the top of which the scraper is drawn and dumped through a grating into a car, cart or wagon. The wheel scraper may be used for longer distances, not exceeding 500 feet. The cost per cubic yard is about 20 cents.

Steam Shovel.—The steam shovel, either continuous with an endless chain carrying buckets with a cutting edge or intermittent like the usual

steam shovel. These are made in various sizes, handling from 400 to 5,000 cubic yards per ten hours. For cement works the smaller shovels handling from 400 to 800 cubic yards in ten hours will be of sufficient capacity. If the steam shovel is to be used for shale the bucket must be provided with sharp steel teeth for first cutting the shale, after which the material is shoveled into the car. The bucket capacity should be ¾ or 1 cubic yard. The cost of winning material by this method is probably from 5 to 12 cents per cubic yard.

Dredging.—Dredging is practiced in obtaining clay from river or lake bottoms or in very wet, low country, as in the lake region of Michigan and Indiana. It would seem that for this work a continuous bucket dredge would be preferable to the ordinary dipper dredge, as it would enable the manufacturers to dredge deeper. The writer has, however, seen a barge dipper dredge working to a depth of thirty feet without any difficulty. The cost of dredging in this manner is not great, probably not over 4 cents per cubic yard of 58 per cent. moisture, which is equivalent roughly to 1¾ barrels of cement.

Mining.—Mining is practiced only where absolutely necessary, and is not carried on at any cement works to the knowledge of the writer, though there is no reason why it should not be undertaken if necessary. In mining, the main requisite is a strong thick stratum overhead, preferably sandstone. A clay roof is dangerous and causes expensive mining. The cost of mining is always heavy, from 50 cents to 75 cents per ton, depending on the thickness of the vein, nature of roof and floor, hardness of the rock, mechanical aids available, etc. The cost of the dead work, track, posts and timbers is about 25 cents per ton, varying with the locality, etc.

WINNING OF LIME MATERIALS.

The methods of winning the calcareous materials according to their character may be classified as:

1. Quarrying.
2. Dredging,
3. Steam shovel work.
4. Mining.

Quarrying.—Quarrying is applied, of course, only in working limestones or cement rock and needs no detailed description. Power drills should be employed, worked either by compressed air, steam or electricity. It is rather difficult to give general figures of the cost of quarrying, but probably 20 cents per ton is not far from the truth.

Dredging.—Dredging is practiced in winning the calcareous marls of Michigan, Indiana and Ohio. The amount of high calcium marl required for one barrel of cement varies from 8 to 12 cubic feet, with

a moisture content of from 50 to 70 per cent.; 10 cubic feet may be safely taken as the average. In prospecting a marl deposit, it is extremely important to make numerous borings in order to calculate the available marl. Owing to the extreme variations which this material is liable to show, it is quite deceptive, and often the variation is far greater than appears on superficial examination. Neglect to look this over carefully has necessitated the closing down of more than one marl plant. In Michigan the marl area controlled by a single cement plant varies from 260 to 2,000 acres.

Steam Shovel. —The steam shovel cannot be employed, as a rule, for winning limestone, though the writer has seen one most powerful machine at work at the Edison Portland Cement Company. In this case a cement rock is being worked by blasting, the machine taking up the loosened material. Calcareous material, of a soft nature, like dry marls, chalk or soft limestones can be worked very economically by means of the steam shovel, and the cost will not be much more than 5 cents per cubic yard.

Mining.—What has been said in regard to clays applies also here, excepting that limestones would be less difficult to mine, owing, as a rule, to the better roof available and the more stable character of the pillars. But the cost, though not as great as for clay, would not be very much less, probably not less than 40 cents per ton.

HAULAGE OF RAW MATERIALS TO WORKS.

There are available four means of conveying the raw materials to the works, which are:

1. Tramways.. { Cable / Electric locomotive / Steam locomotive.
2. Aerial cableways.
3. Transportation by water.
4. Pumping.

The method of haulage to be adopted depends on the distance to be covered, the quantity to be conveyed and the topographical conditions.

Tramways.—Cable tramways are suited only for short distances and are especially useful in dealing with heavy grades. For larger capacities the rope should be endless so as to keep cars going steadily in one direction. Where the grade is sufficient in the right direction, a gravity system can be installed, the loaded cars pulling up the empty ones. It is unnecessary to go into details of construction of such plants, since these have been thoroughly worked out for mining work and such a discussion would be beyond the scope of this report. The distance should not exceed about 1,500 feet. Electric and steam propelled locomotives are adapted

specially to longer haulages, distances up to three miles not being infrequent in this kind of work. For short distances, animal power can be employed in plants with a capacity up to 500 barrels per day.

Aerial Tramways.—Aerial tramways are only advisable for locations with an extremely rugged topography, since they are expensive to construct and to maintain. They are useful, however, where rivers or valleys are to be crossed. We must distinguish between the single moving rope cableway, which supports and moves the load at the same time, and the double cableway, which has two or more supporting ropes and an endless pulling rope. The former can carry single loads up to 200 pounds, has a capacity up to 200 tons per day, and may be built as long as 1½ to 2 miles. The second class of cableways is used most largely These cableways are provided at the terminals with devices for loading and discharging, also with the driving gear for moving the traction rope and brakes. The intermediate supports are of wood or steel. The cars are simply buckets provided with wheels which run on the heavy supporting rope, and a friction grip for attaching to the pulling rope. These buckets may hold a load up to 1,400 pounds, and the pulling rope may have a speed of from 150 to 350 feet per minute. The economical limit of length is probably two miles. The cost of construction is from $5,000 per mile up. As to the power required, this differs, of course, quite widely, and depends on many factors.

One formula given requires for n, the horsepower necessary,

$$n=\frac{qu}{270}\left(\frac{l}{100}(2+0.005(100-qu))\pm h\right)+N_0.$$

Where l is the length of the cableway in meters,

qu=the quantity to be hauled in tons per hour,

h=the difference in level of the terminals, plus for upgrade, and minus for downgrade.

N_0=a constant, varying from 0.5 to 5, allowing for friction. The capacity of double cableways is from 200 to 1,000 tons per ten hours.

Transportation by Water.—Transportation by water is employed especially where the lime material is dredged or where located on a suitable waterway. This affords a very cheap method of transporting large quantities of material.

Pumping.—Pumping is frequently practiced in dredge work where the dredged material is mixed up with more water and made up into a slurry containing about 60 per cent. of water by means of a pug-mill, the material having been run through a stone and root separator, which is simply a perforated revolving cylinder. At the works of the Peninsular Portland Cement Company, the slurry is pumped from the dredge to the works, the pipe having a flexible connection, and being supported

by stakes driven into the lake bottom. This is applicable only where deep dredging is practiced, the dredge being moved but slowly. At other marl plants the dredged marl is taken by means of scows to the mill and pumped from the scow into large reservoirs. The slurry is forced along the mains by compressed air; this being far superior to the work of plunger pumps. The writer has seen in Germany clays handled by stirring up with water in agitators, screening, and then pumping for distances as great as two miles. In this way, coarse sand, roots, etc., are at the same time removed completely.

Wherever solid material is being hauled, it should be dumped into large bins with steep iron-sheeted bottoms from which the rock can be allowed to drop into the chutes leading to the crushers. One man can thus feed a large quantity of material with but slight effort. The gates for controlling the flow of heavy, coarse material from bins are heavy plank affairs, with a few heavy iron teeth which will stop the sliding of the material with the greatest ease.

GRINDING OF RAW MATERIALS.

In the United States we must distinguish clearly three modes of preparing the raw mixtures, depending on the three combinations of raw materials available:

First, the cement rock and limestone combination employed in the Lehigh Valley, Pennsylvania.

Second, the limestone and clay mixtures wherever suitable limestone and clay is found.

Third, the marl and clay mixtures used in Michigan, Indiana and northern Ohio.

It becomes at once evident that the first and second, working with dry and hard material, must employ practically the same class of preparing machinery, while the materials of the third combination naturally call for machinery adapted to working them in the wet state, though, of course, this becomes optional to some extent, since the slurry may be dried at once, and then worked dry. But this is not the regular procedure, especially in working with rotary kilns.

Preliminary Dryers.—Frequently the clay or the limestone or both must be dried before they can be taken through the grinding machines. This is accomplished by means of rotary dryers which consist essentially of a revolving brick-lined iron tube, 40 feet long and 54 inches in diameter, revolving on two sets of carrying rollers and driven by a train of gearing. Heavy steel tires made in halves are attached to cast iron riding rings riveted to the shell. The heat is produced by an ordinary furnace fired with coal like a boiler furnace, the heated combustion gases and air passing through the tube and out into the stack. The materials to be

Fig. 31. Rotary dryer for preparing clay and stone for fine grinding. As constructed by Allis-Chalmers Company.

dried are charged at the stack end and discharged, hot, at the furnace end. The capacity of such a machine is from 5 to 10 tons per hour, depending on the condition of the material and the amount of moisture contained by it. It requires from 4 to 6 horsepower for operation. Owing to the fact that this machine discharges the dried material when still hot and the gases leave the machine far from saturation it is not the most economical type of dryer. Other systems, like the Cummer dryer and others, make better use of the heat, but at the same time are more troublesome to operate. The dryer shown by the accompanying illustration is a simple and, mechanically, an efficient machine, though not the most economical type. It is, however, to be preferred to any complicated system in which the heat efficiency is counteracted by mechanical difficulties.

ROUGH CRUSHING MACHINES.

The dry materials require three kinds of preparing machinery:

1. Rough crushing machines,
2. Intermediate grinding machines,
3. Fine grinding machines.

These three operations must be clearly kept in mind, as they cannot be carried on successfully at one and the same time.

Of the rough grinding machines two types are employed, known generally as the jaw and spindle crusher respectively. In addition another type is employed, as far as the writer knows, only in one instance, namely the roll crusher.

Jaw Crusher.—Under the type of jaw crusher we understand a number of machines, which though they differ in regard to the movement of the jaw, or in the number of jaws employed, yet employ the one general principle. Thus, we know the Dodge breaker, the Buchanan, the Duplex breaker, the Forester, the Kron, the Sturtevant and others. The Blake crusher is considered typical. Its action is simply the opening and closing of steel-faced iron jaws, moved by toggles which are set in motion by a vertical eccentric motion. A seven inch by ten inch Blake crusher has a movement at the mouth of 0.78 inch, at the throat of 0.25 inch, and makes 275 revolutions per minute. As a piece of rock is seized by the jaw, it is gradually crushed to a smaller and smaller size and worked down towards the throat, the width of which governs the size to which the rock is broken. The fixed and the swing jaw plates are often made of the hardest steel obtainable, chrome or manganese steel; if these are not used, chilled iron is found to be the cheapest. In work of this sort the most essential requirement is, of course, that the machine be amply strong enough for the strains it has to withstand, even if this should be accomplished at the cost of some of the capacity. They should be able to take the largest lump and reduce it without the necessity of breaking up with a sledge. The cost of crushing with a jaw crusher has

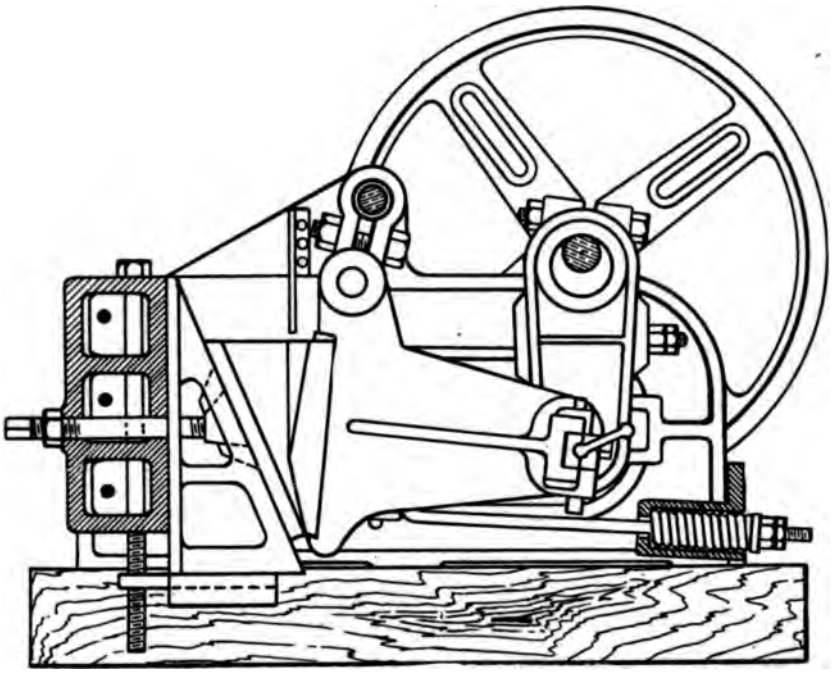

Fig. 32. Jaw crusher of the Blake type.

been assembled by Prof. Richards, in his work on Ore Dressing as follows:

Size of mouth in inches	4 x 10	7 x 10	9 x 15	10 x 20	13 x 30
Tons crushed in 24 hours	84	120	192	300	540
Horsepower	5	8	12	20	30
Cost of breaker	$275	$500	$750	$1,050	$2,250
Cost in cents per ton for oil	0.021	0.021	0.021	0.021	0.021
Cost in cents per ton for interest and depreciation	0.106	0.135	0.127	0.114	0.135
Cost in cents per ton for labor	4.762	3.333	2.083	1.333	0.741
Cost in cents per ton for power	0.773	0.865	0.811	0.865	0.721
Cost in cents per ton for wear	0.815	0.815	0.815	0.815	0.815
Cost in cents per ton for repairs	0.462	0.462	0.462	0.462	0.462
Total cost in cents per ton	6.939	5.631	4.319	3.61	2.895

These estimates, however, are based on hard materials and hence are rather higher than the cost of crushing limestone.

Spindle Crushers.—These machines differ from the jaw crushers inasmuch as the crushing is continuous, being done by a gyrating vertical spindle, whose upper part has the shape of a truncated cone and which is set in motion by means of a bevel gear. The cone rotates within a conical space representing an inverted cone. As long as the machine is empty the spindle rotates, though it could assume a gyratory motion. But as soon as rock is fed between the crushing surfaces the spindle follows an eccentric just beneath the bevel wheel. This causes the head to approach and recede from the concave grinding surface of the shell surrounding the cone, the movement at the bottom of the truncated cone being greater than at the top. The result is a crushing action by pressure which has a greater movement upon the smaller lumps than upon the larger. The fulcrum of the machine is located at the bottom of the upper journal of the spindle. A lump thrown into the machine is broken, drops, catches again, is again broken, and thus continues on its way down. The fineness of the output can, of course, be regulated by regulating the width of the throat.

Professor Richards gives the following table showing the cost of crushing by spindle breakers:

Size of mouth, in inches	4 x 30	6 x 42	8 x 54	11 x 72	18 x 126
Tons crushed in 24 hours	72	216	540	1,080	3,000
Horsepower	3	9	22	45	125
Cost of breaker	$375	$760	$1,800	$3,300	$7,000
Cost in cents per ton for oil	0.021	0.021	0.021	0.021	0.021
Cost in cents per ton for interest and depreciation	0.169	0.114	0.108	0.099	0.076
Cost in cents per ton for power	0.541	0.541	0.541	0.541	0.541
Cost in cents per ton for labor	5.556	1.852	0.741	0.370	0.133
Cost in cents per ton for wear	0.971	0.971	0.971	0.971	0.971
Cost in cents per ton for repairs	0.308	0.308	0.308	0.08	0.308
Total cost in cents per ton	7.566	3.807	2.678	2.310	2.050

Comparative tests of the Gates Iron Works have shown the following results in crushing a hard granite with a crushing strength of 30,000 pounds per square inch, in lumps as large as the machine would take.

The Blake crusher represents the jaw crusher type, the Gates the spindle crusher type.

Details of Contesting Machines

Kind of machine.	Mouth size, inches.	Width of throat inches.	Movement at throat, inches.	Revolutions of driving pulley per minute.	Kind of shoe.	Kind of die.	Material used, Lbs.	Time required, minutes.	Capacity per hr. Pounds.	Net power used, H. P.	Relative work used in crushing.
Gates, No. 0	4 x 33	0 9375 to 1	0.3125	500	Corrugated	Smooth	1,000	3.33	18,000	5.2	100
Blake	4 x 10	0.8125 to 0.875	0.3125	250	Corrugated	Corrugated	1,000	5.33	11,200	6.1	187
Gates, No. 3	7 x 48	1.5 to 1	0.5	450	Corrugated	Smooth	2,000	2.66	45,000	21.7	100
Blake	7 x 10	1.25 to 0.75	0.5	250	Corrugated	Corrugated	2,000	6.66	18,000	12.45	144

Sizing Tests of Products of Spindle and Jaw Crushers.

	On 2.5 inch.	Thro 2.5 and on 2.0.	Thro 2.0 and on 1.5.	Thro 1.5 and on 1.0.	Thro 1.0 and on 0.75.	Thro 0.75 and on 0.5.	Thro 0.5 and on 0.25.	Thro 0.25 and on 0.125.	Thro 0.125.	Total.
Gates 4 x 33	3.0	5.3	24.2	35.0	9.9	8.4	6.3	3.2	4.7	100
Blake 4 x 10	7.0	10.0	23.0	23.2	6.4	9.9	8.7	4.5	7.3	100
Gates 7 x 48	5.0	17.5	27.0	20.8	6.7	7.3	9.0	2.7	4.0	100
Blake 7 x 10	6.5	23.0	21.1	17.8	4.8	7.9	8.2	4.1	6.6	100

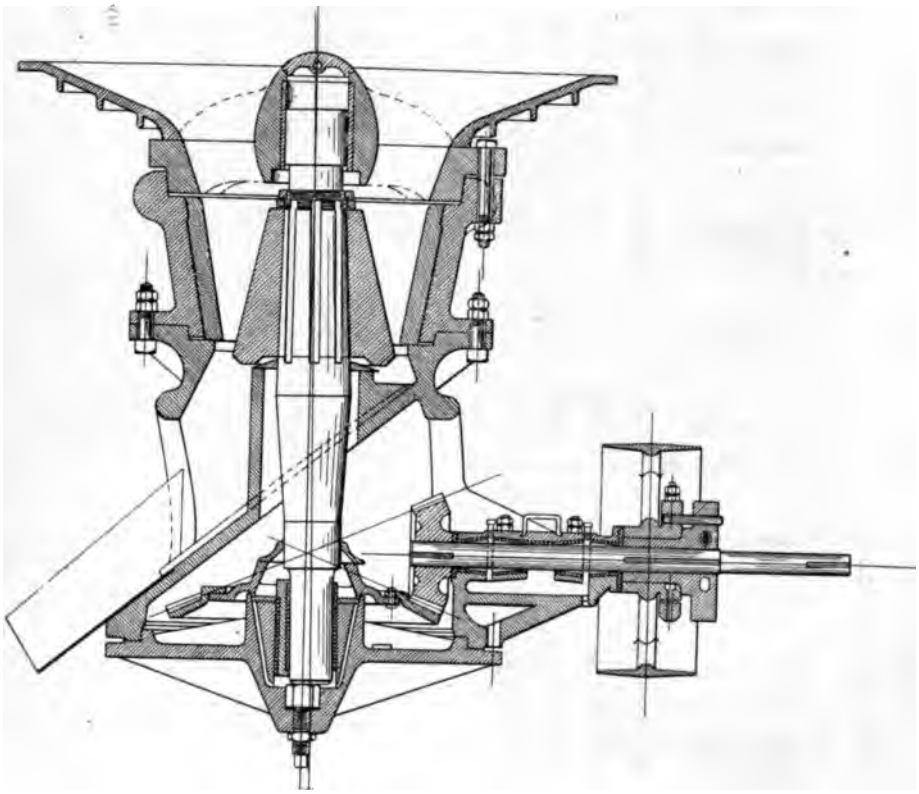

Fig. 33. Spindle crusher, Gates type.

In these tests the Blake crusher was handicapped by its small size and the smaller width of throat. The general tendency seems to be in favor of the Blake crusher for small and in favor of the Gates for greater capacities. The continuous action also is in favor of the Gates crusher.

In cement practice a rock crusher with an average capacity of 25 tons per hour requires under conditions of maximum load 33 horsepower and an average of 20 horsepower.

Rolls.—These are two iron cylinders revolving on shafts in the direction indicated by the arrows in the accompanying diagram acting upon the lump of material *c* on the principle of a toggle joint. The rolls are held in position by the journals acting radially upon the lump and gradually drawing it down to the narrowest space. The material is broken by true crushing by virtue of the superior crushing strength of the cast iron. The rolls consist of a core of soft iron which carries a shell

of chilled iron. One shaft revolves in fixed, the other in movable boxes. The movable ones are held up toward the fixed boxes by means of powerful springs, or also by levers and weights. Power is usually applied by means of gears and pulleys. The shafts are of mild steel.

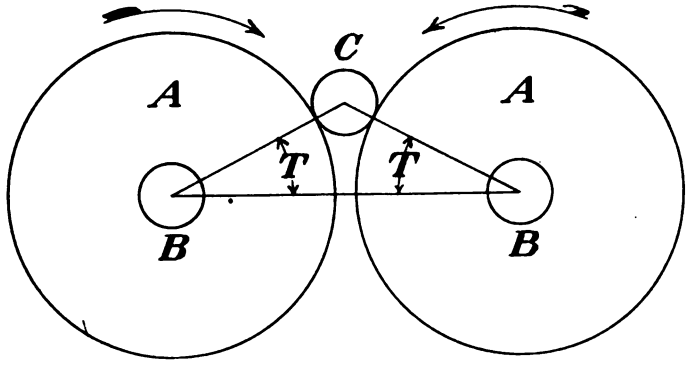

Fig. 34. Diagram illustrating the operation of crushing rolls.

As has been said, rolls are not typical rough grinders, being used only by the Edison Portland Cement Co. These are 5 feet in diameter, with 5 feet face, and are provided with striking pieces, pyramidal in shape, 4 inches high. Below these large rolls smaller ones for intermediate grinding are arranged, 3 feet in diameter and 3 feet long. The rolls make about 150 revolutions per minute. The journals are, of course, extremely heavy. Both rolls are driven by pulleys direct. These may run loose on the shaft, but not until they have overcome the friction of band brakes, which are held up by springs with great tension. These rolls can take a charge of about 5 tons, and the capacity when running 150 revolutions per minute is approximately 300 tons per hour. However, on dumping in a charge, the speed is decreased and it takes some time to pick up again, requiring about 80 horsepower to do this. This change of retardation and acceleration takes up about one-sixth of the time. The average power consumed is 55 horsepower. The distance between the striking knobs is 10 inches.

INTERMEDIATE GRINDING MACHINES.

Of machines of this kind we have the following types:

1. Rolls.
2. Disintegrator.
3. Kent mill.
4. Ball-mill.
5. Dry pan.

Rolls.—It cannot be said that rolls are now used in American cement works with the exception of one, but their general efficiency

for this purpose is so promising that the writer has given them first place in this classification, since it appears to him that these machines do the work of intermediate grinding at the lowest cost. Rolls should not be fed with material over 1½ inches in diameter. It is not an easy matter to give the best size for rolls intended to prepare material for fine grinding, since the velocity, the size of the feed, and the character of the material to be ground are important factors. One large manufacturer of rolls gives 24x14 inches, another 26x14 inches as the best standard rolls. As a whole, larger diameters are to be preferred, since the increased surface means a greater capacity and since they can make a greater reduction with one passage and lastly because they can be run at a greater speed owing to their favorable angle of nip. Yet there must be considered the fact that two small rolls cost less, give a more uniform output, are cheaper to run, and repair and wear more uniformly. But it seems they should not be less than 24 inches in diameter for cement work. The width varies from 12 to 16 inches. Narrower rolls are easier to keep true and by running them faster may have the same capacity as wider rolls. The average peripheral speed of many rolls was found by Professor Richards to be 379 feet per minute, and the average velocity of rolls crushing breaker products 345.7 feet per minute. With a peripheral speed of 300 feet a 24-inch roll would have to run 48 revolutions per minute; with a speed of 400 feet, 64 revolutions.

There is a tendency to advocate high speeds in rolls, as higher speeds make the rolls run more smoothly, and make the action more "free" crushing, and also to use diffffferential rolls, one running faster than the other. Differential rolls have been used to some extent and the experience seems to be that for hard crushing like quartz, differentiation does not help much, but that for limestone and clay the case seems to be different. In one instance, one roll running 25 per cent. faster than the other prevented the formation of ribbons, that is, pressed flakes, while the wear was slightly more, but much more uniform.

The shells have been made of various materials, chilled cast iron, cast steel, chrome steel, hammered steel, manganese steel, rolled steel and forged steel. Chilled iron is cheap, but pits and wears rapidly, chips and is hard to true up. Cost, 2 to 4 cents per pound. Cast steel costs from 6 to 6½ cents per pound, but its surface is not very reliable. Forged steel is the most reliable material and wears uniformly with some attention. Cost, from 6½ to 10 cents per pound. The chrome steel is said to be still better; cost, 10 cents per pound. It is important that the rolls be kept smooth and parallel. This is done by setting the rolls with different laps at the end of every day, say ¼ on one end on one day and the same amount at the other end the following day, and turning them down or grinding the surface with emery. This can frequently be done with the rolls in place. If duplicate rolls are used, one can be used while the other is trued up, the changing taking but little

time. This is a considerable advantage over ball-mills or more complicated apparatus. Also when the rolls used for finer crushing have been worn they may be placed in position as coarse rolls. The rolls are held in position by car-wheel springs or rubber blocks, the latter being, however, not suitable for heavy use. The pressures exerted by these springs are indicated by the following table:*

Length of spring in inches.	Amount of compression, in inches.	Pressure exerted by the two sets of springs in pounds.	
		On 26 inch roll.	On 24 inch roll.
7.9375	0.0.	0	0
7.4375	0.5	15,000	22,500
6.9375	1.0	30,000	37,500
6.4375	1.5	41,250	52,500
5.9375	2.0	48,750	71,250

The rolls are driven either by direct belting or by belts and gears. For slow speeds the gears are preferred, for higher speeds the belts.

In working with rolls it is absolutely essential that the material to be ground be fed uniformly, and hence the rolls must be provided with simple but efficient feeding devices. The quality of crushing depends to a great extent on the way they are run. When run slowly the material may be crowded so that the fine particles cannot separate from the coarser, and hence are reduced some more by abrasion upon each other. This is called "choke" crushing.

When the speed is increased the fine matter is removed as fast as formed; this is called "free" crushing. This is the usual and most satisfactory method. The power required differs, of course, with the size and work done. On an average according to Richards it is 10 horsepower for 100 tons in 24 hours. The cost of crushing is from 3 to 6 cents a ton for limestone, not including the truing of the shells.

In regard to the space between the rolls, which may be from nothing up to ¼ inch, the angle of nip plays an important part. For coarse rolls, a rough rule says that the distance should be one-half the diameter of the largest lumps fed.

The angle of nip is one-half of the angle made by the tangents to the rolls, at the points of contact *aa*, between the lump of rock, *e*, assumed to be a sphere, and the rolls. These tangents form the angle 2n,

*R. H. Richards, Ore Dressing, p. 74.

half of which is called the angle of nip. If the lump is as large as the space between the rolls, the angle is, of course, zero, increasing until the angle is so large that the rolls cannot nip the rock. The angle is a function of the diameter of the rolls, the diameter of the lump and

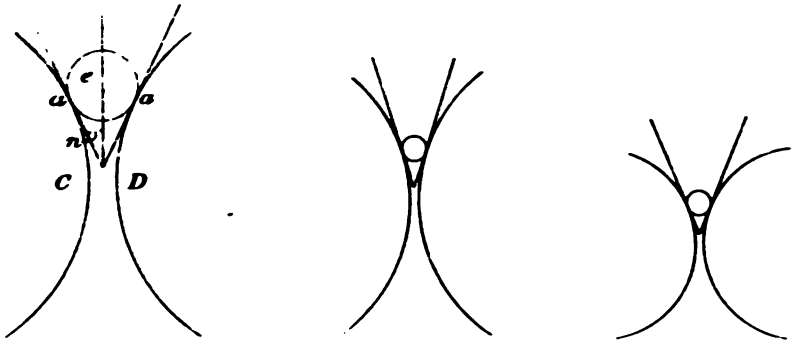

Fig. 35. Diagram illustrating the angle of nip of rolls.

the distance between the rolls. It is diminished by increasing the diameter of the rolls, by increasing the space between the rolls and by decreasing the size of the lumps.

If b=the radius of the sphere to be crushed,
a=½ the space between the rolls,
n=the angle of nip,
and r=radius of the roll=½ diameter,

$$\cos n = \frac{r+a}{r+b}.$$

In practice the angles of nip are found to be from 4° 16′ up to 24° 5′, with, according to Professor Richards, an average of about 13° 30′.

The standard angle of nip is given as 16°, which should not be exceeded. Angles smaller than this will have still more favorable action, which, however, is unnecessary. In the following tables the relations between the diameter of rolls, the size of feed and the space between the rolls when the angle of nip is 16°, as given by Richards, are quoted in the table on page 263.

In preparing for the tube mills, the material coming from the breaker should at least make two passages through the rolls, which should not be less than 24 inches in diameter and 12 inches wide. In the accompanying cut, figure 36, rolls are shown which prepare material for the tube mill, taking the crushings of a breaker, but requiring that these should not be more than ¾ of an inch in size. This machine has two feed rolls, which distribute the material uniformly over the surface of the roll. Two curved sheets of iron deliver the

Size of Particles, in Inches, Nipped by Rolls of Various Diameters Placed Various Distances Apart,

Diameter of rolls in inches.	Space between the rolls in inches.						
	0.75	0.625	0.50	0.375	0.250	0.125	0.
36	2.23	2.10	1.96	1.84	1.71	1.57	1.45
30	1.99	1.86	1.73	1.60	1.47	1.34	1.21
26	1.83	1.70	1.56	1.44	1.31	1.17	1.05
24	1.74	1.61	1.48	1.36	1.22	1.10	0.96
20	1.58	1.46	1.32	1.20	1.06	0.94	0.80
16	1.42	1.29	1.16	1.03	0.90	0.77	0.64
9	1.14	1.01	0.88	0.75	0.62	0.49	0.36

Distance Between Rolls, When Diameter and Size of Particles to be Crushed are Known.

Diameter of rolls in inches.	Size of feed in inches.					
	1.50	1.25	1.00	0.75	0.50	0.25
36	0.046		–			
30	0.280	0.038				
26	0.432	0.191				
24	0.512	0.270				
20	0.666	0.424	0.031			
16	0.822	0.580	0.185			
.....	....	....	0.340	0.101		
9	1.193	0.851	0.613	0.372	0.132	

material at the proper place. The rolls are of chilled cast iron, the lower one, being movable, being held in position by strong springs. The upper roll has a greater peripheral speed, being geared in the desired ratio. In the construction of this mill the ratios 1 :1.5, 1 :2, 1 :2.5 and 1 :3 are carried out. The capacity of this machine is on the average 8,200 pounds, or 23 barrels per hour, and it requires from 8 to 12 horsepower.

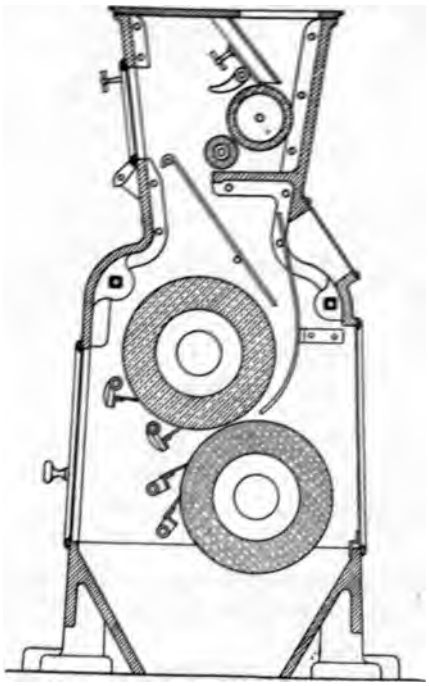

Fig. 36. Intermediate rolls, with feed rolls, for ¾ inch material.

It must be repeated that for satisfactory results in intermediate grinding two passages are required, which, however, may be accomplished by means of one set of three rolls, illustrated in figure 39, representing the Edison three high rolls.* These are 36 inches in diameter, 30 inches face, and run 90 revolutions per minute. The shaft L is driven by wooden-toothed beveled gears running in oil. The upper two rolls are driven by friction from the lower and have boxes that are free to slide in vertical guides. Loose sheaves, F, over which run seven passes of ½-inch wire rope, a bight of the rope passing over the pulley, J, provided with a piston tightener, K, driven by compressed air, furnishes a pressure of 125,000 to 150,000 pounds for crushing. These ropes eliminate nearly all friction except that due to the weight of the three rolls, which amounts to 20,000 pounds. The shells are of soft gray cast iron, costing 2 cents per pound. The edges are beveled to prevent chipping. Each shell is a true cylinder, inside and outside, and is keyed in place. It is 8 inches thick when new and weighs 4,500 pounds. It has to be trued every three days, steel tools being used for truing. The wear of the shells is 0.25 cent per ton. A roller feeder, s, is used. The coarser set of rolls crushes 300 tons of ½-inch material per hour to pass a 14-mesh screen (0.060x0.5-inch slot).

*R. H. Richards, Ore Dressing.

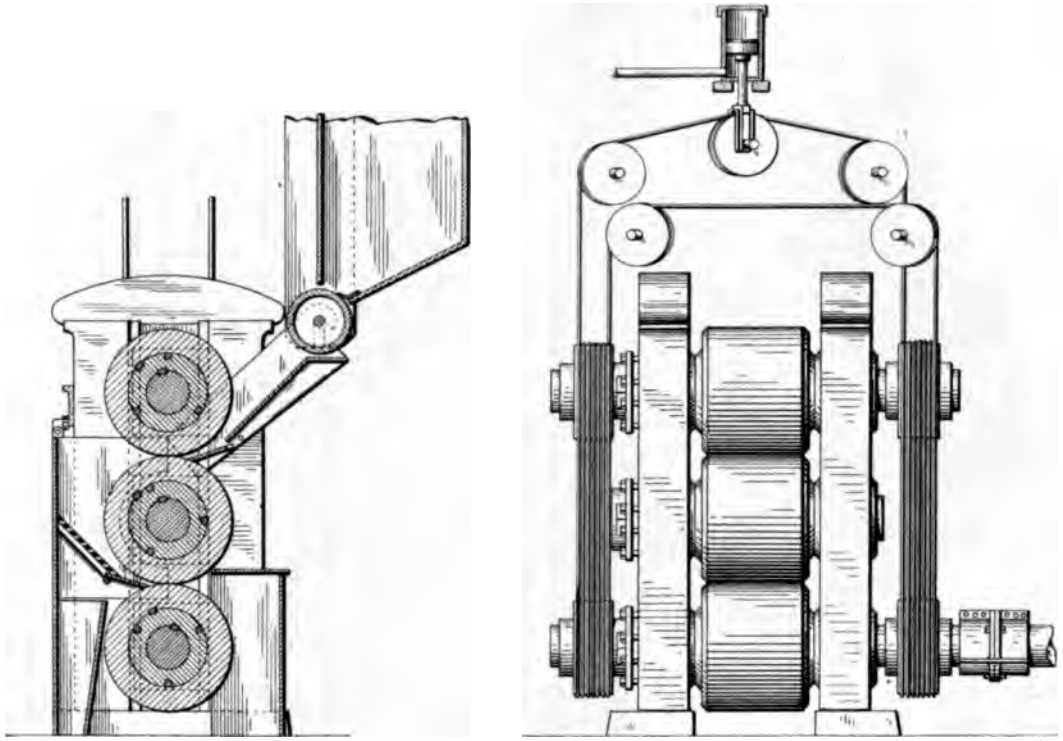

Fig. 37. Three-high rolls of the Edison Portland Cement Company.

The oversize comes back at the rate of 200 tons per hour, making the amount handled 500 tons per hour. The fine rolls crush the 14-mesh material and reduce it to 1-50 of an inch screen at the rate of 135 tons per hour, to which is added the oversize which is returned to the rolls.

Each set of these mills requires power as follows, No. 6 being the coarser and No. 7 the finer rolls:

	When empty, horsepower.	Crushing horsepower.
No. 6 rolls	10	260
No. 7 rolls	10	150

Edison thus does both the intermediate and fine grinding with rolls.

Disintegrators. —These are true impact crushers and consist essentially of several cages of round bars revolving in opposite directions. The material is fed at the center, is struck by the bars of the inner cage and partly broken and takes a direction tangential to this cage, when it is struck by the bars of the second cage, revolving rapidly in the opposite direction. This type of machine is represented by the Stedman mill and other later makes. By means of a bar projecting into the inner mill, lumps or cakes forming on the inside are broken up. The machines vary in size from 30 to 50 inches, and the bars are from 1 to 1¾ inches in diameter, according to the size of the machine. This machine is well suited for handling almost dry clays, soft shales and coal, for which materials it has a great capacity and is very efficient. It is not so well adapted to heavy grinding. A 40-inch machine will grind 175 to 200; a 50-inch, 350 to 400; a 60-inch, 500 tons of coal per day, requiring 35 to 50, 70 to 100, 100 to 125 horsepower. A 36-inch mill will grind from 90,000 to 140,000 pounds of clay per day, requiring 12 to 15 horsepower; a 40-inch mill will prepare 150,000 to 200,000 pounds of clay, requiring 15 to 20 horsepower.

For heavier work the pulverizers of the hinged hammer type are employed (see figure 38,) and have in a number of cases proven quite successful. In one plant the crushings from the rock breaker 1½ inches in size are taken and reduced so that 84 per cent. passes a 20-mesh sieve, by a Williams pulverizer, showing a capacity of 137 tons in 11 hours, with a consumption of about 75 horsepower. The material is a mixture of limestone and shale. These machines, unlike the Stedman type, do not consist of several cages, but simply of hinged hammers

which revolve around a horizontal shaft, this type of machine being evolved from the simple chain mills which were used some 20 years ago for preparing brick clays in Minnesota and other Western states. The chain mills consisted of heavy chains fastened to a revolving shaft which

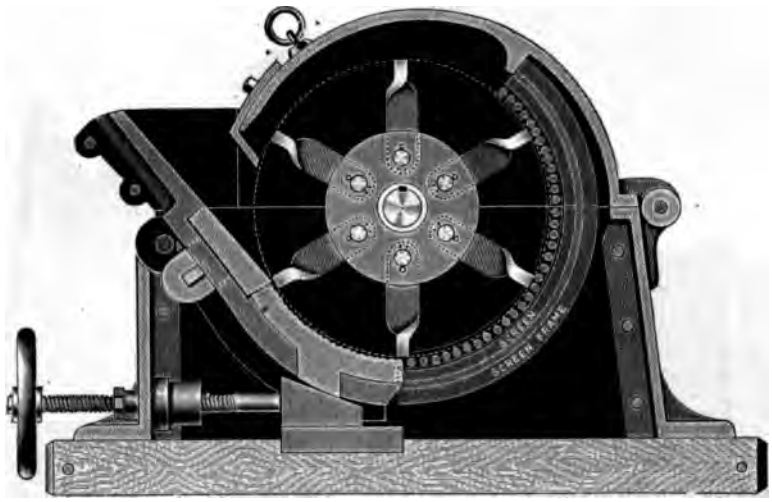

Fig. 38. Disintegrator of the hinged-hammer type, as made by Williams.

whipped the material into small particles. From the standpoint of work accomplished these old homemade mills were quite efficient, but the construction was imperfect in many cases and gave considerable trouble, as was to be expected. The Williams mill, though subject to greater wear than the rolls, and also more expensive as to cost of repair, is a very efficient machine for limestones which are not too hard and dense. When equipped with water-cooled journals, it can work hot materials right from the rotary dryer.

Kent Mill.—This mill (see figure 40) consists essentially of a revolving ring and three rolls pressing against its inner face. The rolls are convex and the ring is concave and tracks on the rolls. Springs support the rolls yieldingly and the rolls support the ring so that the four crushing parts are free to move. The material falls from the inlets on to the inner face of the ring. Centrifugal force holds it there in a layer an inch deep. It revolves with the ring and passes under the rolls. The latter are pressed by the springs outwardly against the rock on the ring with a pressure adjustable to 20,000 pounds, the adjustment being accomplished by means of the screws against the springs. As the rolls pass over the rock they crush it against the ring, while the crushed rock flows off each side of the ring into the casing and falls to the discharge. It is claimed that 90 per cent. of the rock is abraded on itself in crushing, so that the wear on the parts of the machine is quite slight and there is

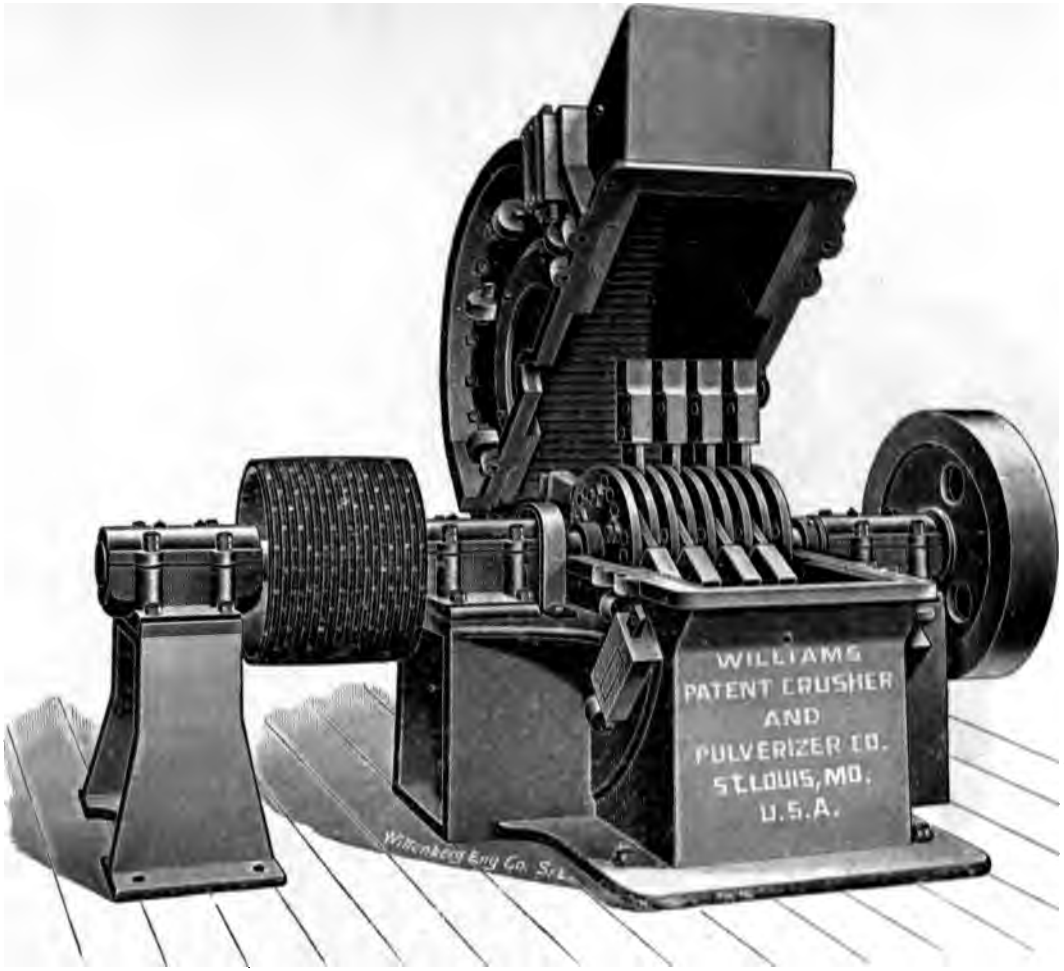

Fig. 39. Williams pulverizer, showing hinged hammers or flails, and grating.

no rubbing on the rock. By attaching separators, either screens or wind separators, to the machine, it can produce material quite fine in size. The speed of the machine is 180 revolutions, its capacity is from 2 to 8

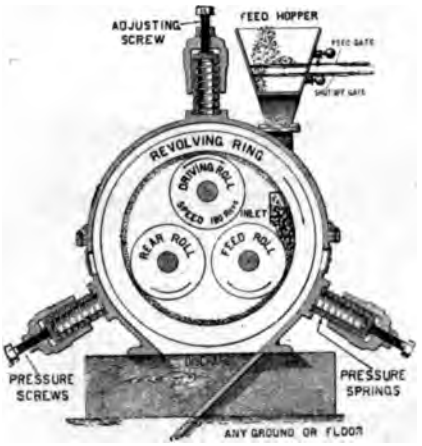

Fig. 40. Cross section of Kent mill.

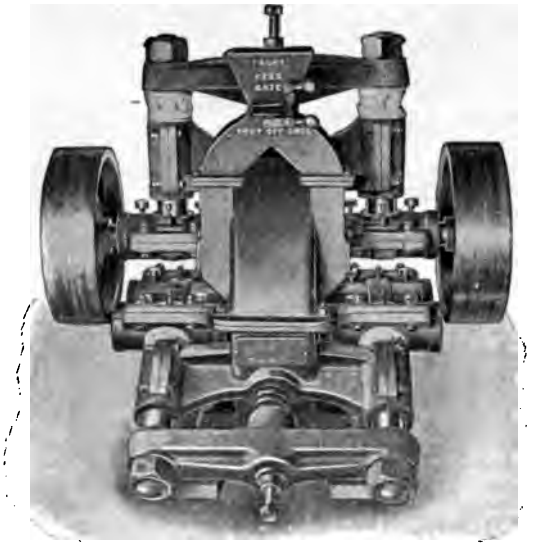

Fig. 40a. Exterior view of Kent mill.

tons per hour according to material and fineness, and the power required is 25 horsepower. In grinding limestone the capacity is quite close to 8 tons per hour, but is considerably less for grinding quartz. The journals

are often provided with water-cooling arrangement, which enables the machine to handle the clinker or material coming from the dryer. The machine, as far as known to the writer, has been very successful.

Ball-Mill.—This mill, in its simplest conception, consists of a cylinder revolving around a horizontal axis with die plates around

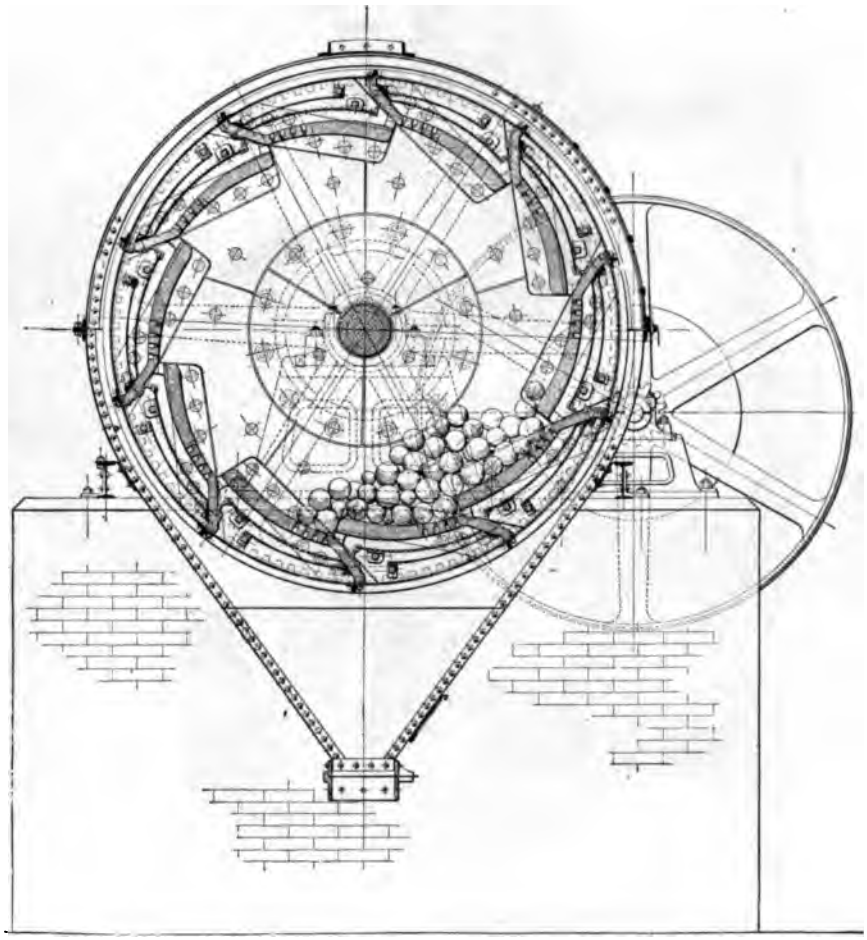

Fig. 41. Ball mill, cross-section.

the circumference. The grinding is done by steel balls. The die ring is composed of perforated chilled iron plates arranged so that each laps the next (figure 41). In this manner steps are formed which give the balls a drop from one to the other, and at the same time the oversize material returned from the screens is admitted into the crushing space at these points. Outside of the die plates coarse screens

are arranged through which the fine material escapes and falls into a collecting bin. The oversize material is caught by deflectors and returned to the crushing chamber. The material is fed through a hopper at one end and leaves through the screens. The machine is also able to do fine grinding if outside of the first screens finer sieves are attached, and the oversize of the fine screens again falls back into

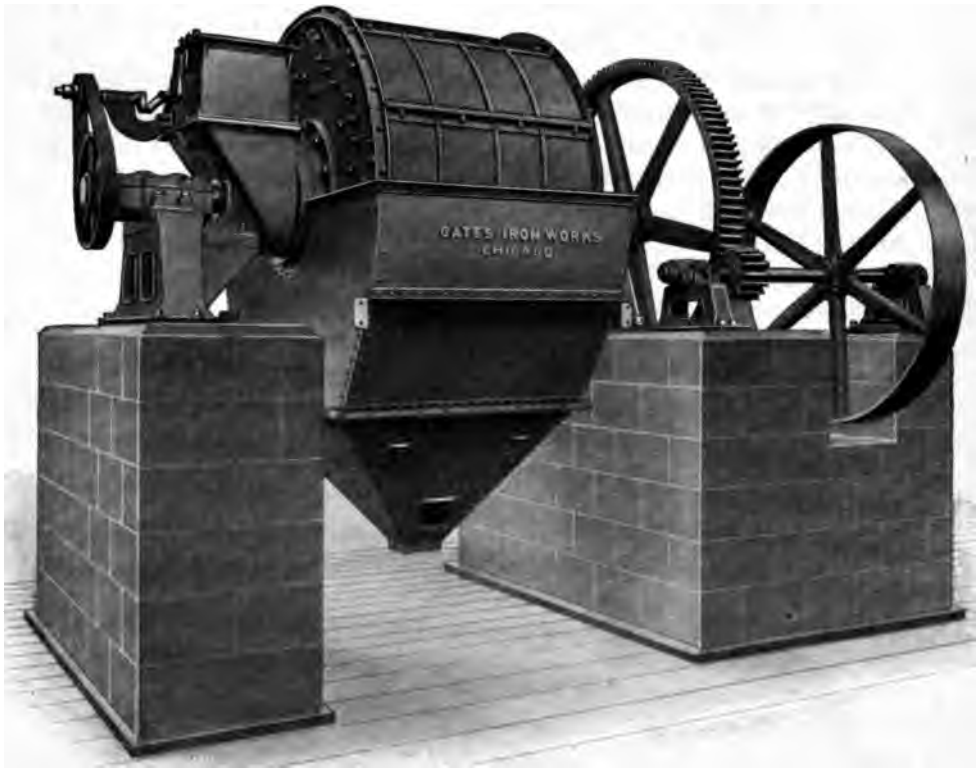

Fig. 42. View of a ball mill, as erected by the Gates Iron Works.

the crushing space. But the capacity is thus decreased very greatly and the efficiency of the machine for this purpose is rather doubtful. The machine, however, works more successfully in this direction if, instead of the screens, there is a strong current of air blowing through the mill, which removes the fine particles constantly as soon as formed, leaving the coarser grains to be ground fine.

The following table gives some data concerning modern American ball-mills, made by the Allis Chalmers Company:

Size No.	Weight without charge of balls. Pounds.	Weight charge of balls. Pounds.	Capacity on Portland Cement clinker. 20 mesh.	Power required.
7	29,500	3,000	12 to 16 bbls. per hour	30 to 40 H.P.
8	41,100	4,500	18 to 24 bbls per hour	40 to 50 H.P.

In starting the mill, from 100 to 120 per cent. additional power is required. When pulverizing to pass all through 20 mesh, from 30 to 40 per cent. will pass a 100 mesh sieve. In grinding limestone, the capacity is greater and averages, for the larger size of mills, 5 tons per hour to 20-mesh sieve. It was found that in grinding 102,400 barrels of cement the steel balls lost 2,959.0 pounds of metal, or 0.139 pounds of metal per ton crushed. At one cement mill in Europe a ball-mill of 64 inches inside diameter, making 17 revolutions per minute, with slits 0.4 inch wide, and requiring 17 horsepower, working a hard limestone, showed an average capacity of 7,700 pounds per hour. At the works of William Krause and Sons, Martin's Creek, Pa., accurate measurements showed the actual average power required to drive one ball-mill to be 39 horsepower. As has been said, some European manufacturers use the ball-mill for fine grinding, separating the fine powder either by means of screens or by blowing air through the material. The first kind is represented by the mill built by Siller and Dubois, in which the first sieve is a steel screen, with one mm. slit perforations, while the fine sieve is a brass screen, 12 meshes to the linear inch. The mill, 64 inches inside diameter, was found to produce with 17 revolutions per minute and 15 horsepower 2,794 pounds of cement per hour, while another mill, of the same make but 72 inches inside diameter, showed an average capacity of 2,970 pounds per hour, requiring 17 horsepower. The fineness of the ground cement is, however, not stated.

The second class of ball-mill with wind separator, having no fine sieves, as built by Pfeiffer, has an average capacity of 1,430 pounds of fine cement, leaving a residue of from 10 to 13 per cent. on a 90-mesh sieve, per hour, requiring 12 to 14 horsepower, or producing 110 pounds of cement per horsepower hour. Since the sieves are very troublesome to take care of and the wind separator does not possess a sufficient capacity, the American practice of using the ball-mill purely as an intermediate grinder without the fine sieves is the best, as it leaves the fine grinding for a typical fine grinding machine. As a type of intermediate grinding machine the ball-mill has the advantage of thoroughly blending the materials, but shows excessive expenditure of power and high repair cost. The fact that it produces 30 to 40 per cent. of fine material does not help the case where this fine size cannot be separated

before feeding into the tube-mill. As a machine it is decidedly inferior to the preceding mills in regard to economy of output.

Dry Pan.—The dry pan, or edge runner, consists of a revolving pan from 6 to 9 feet in diameter, on which run two or more heavy mullers. Around the circumference a space of about 12 inches width is filled with perforated plates. The grinding is done on the solid plate, and the crushed material is scraped on to the perforated plates by fixed scrapers. The oversize material is thrown back on to the center of the pan to be crushed again. This machine is well suited for the intermediate grinding of dry shales and clays, with which a 9-foot pan may show as high a capacity as 100 tons per day, but it is less efficient with hard limestone or soft clays. For softer stones it would show a good output. The iron frame pan does not need much attention and repairs. The chief drawback of the machine is its comparative coarse output, as it cannot be worked with a fine delivery, owing to the danger of choking, and the dust and noise it makes. A 9 foot pan requires from 30 to 40 horsepower.

Arranged in the order of their general efficiency these intermediate grinding machines would range about in the following order: 1, Rolls; 2, Kent mill; 3, Disintegrator; 4, Ball-mill; 5, Dry pan.

FINE GRINDING MACHINES.

Of these we have principally two machines, the tube and the Griffin mill, to consider, the use of other machines, like the buhr or emery mill, having become practically obsolete in American practice.

Fig. 43. Tube mill.

Tube Mill.—The tube mill consists essentially of an iron shell from 22 to 16 feet long and from 4 to 5 feet in diameter, filled somewhat above the axis with flint pebbles, imported mostly from Greenland. The

machine is supported by two heavy, hollow trunnions or shafts at the ends, through which the material is fed and discharged at the opposite end. The pebbles are charged by means of a manhole. A screw feeds the material into the hollow shaft. A wing is also arranged just outside of the mill to prevent any pebbles from leaving the mill at the inlet. At the exit end a screen is attached to the opening to prevent any pebbles from leaving at that end.

Just what the real grinding action is in a tube mill has not been understood clearly until recently, and the views in regard to the apparently simple operation of this mill have not been at all well defined. Recently,* however, the operation of the tube-mill was studied in great detail by means of experimental glass mills, and sections covered at the end with a wire screen. In this manner it was possible to study the motion of the pebbles as well as of the material being ground. One experimental mill was 3 feet in diameter inside and was tried with various speeds of rotation. When at rest the pebbles showed a height of 450 mm. The mill was now rotated with a speed of 23½ revolutions per minute, and it was found that the pebbles rolled down the side rather slowly. On increasing the speed the pebbles seemed to loosen, and they rose to a height of 600 mm. with 32 revolutions. The pebbles have no motion until they are carried up the side of the mill, when at a certain height they become loose and drop back to the bottom, describing a curvilinear path which can be noticed quite distinctly. The pebbles farther away from the surface also do not move with reference to the circumference up to a certain height, but their downward path is more difficult to recognize. On increasing the speed to 35 revolutions the content of the cylinder is loosened still more, so that the pebbles rise to a height of 650 mm.; the downward path becomes quite distinct, and the lower pebbles separate in distinct layers. The pebbles of one layer do not mix with pebbles from the other layers. On speeding up the mill still more the pebbles, at 55 revolutions, form a solid ring around the circumference, without any displacement of the balls. With a speed of 34 revolutions a hollow, kidney-like space was observed.

When material is to be ground it assumes the same motion as the pebbles, distributing itself within the spaces so that it is densest where the pebbles are closest, and looser where the latter are loose. The kidney-shape space, therefore, is free from the material—*no rubbing and rolling between pebbles and the charge takes place anywhere except at the point where the pebbles strike the surface on falling from the highest point.* There the pebbles strike with great force and exert an action similar to that of a stamp mill. The pebbles, climbing up the side of the mill, drop away from it as soon as the vertical component of the forces acting upon it is equal to the centrifugal force, or

*H. Fischer, *Zeitschrift des Vereins Deutscher Ingenieure.* No. 13, 1904.

$$mg \sin a = \frac{mv^2}{r},$$

The curvilinear path, therefore, conforms to the equation*:

$$y = x\frac{\cos a}{\sin a} - x^2\frac{g}{2v^2\sin^2 a}$$

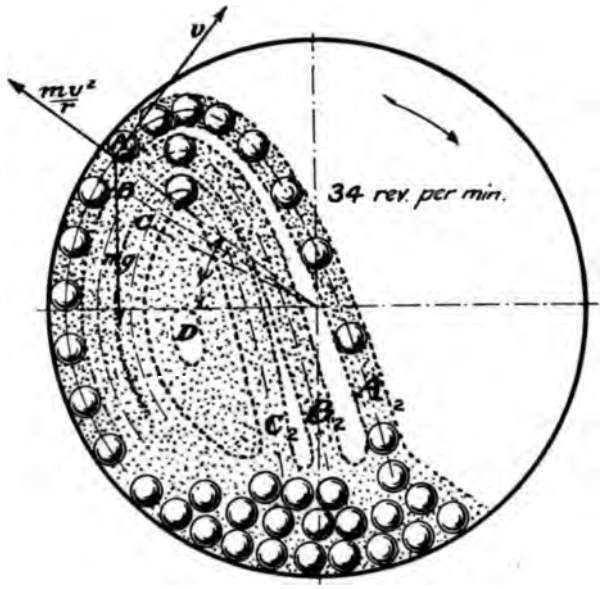

Fig. 44. Diagram illustrating action of tube mill, after Fischer.

In the accompanying figure this path is the line AA_1A_2. The vertical velocity has negative acceleration, becomes zero at A, and hence the pebbles approach each other, touching at A. The charge is thus forced aside at this point and the path must differ from the theoretical curve owing to the collision of the pebbles. After reaching A the pebbles follow the curve with accelerated velocity, and hence the intervals between them become larger. A second layer of pebbles begins its curvilinear path at B, a third at C, etc. These curves are bound to be less clearly defined, but they frequently separate from each other so markedly that it is possible to see through between them. Most of the grinding effect is thus produced at A_2, where the motion of the particles to be ground is the resultant of the vertical velocity and the forward motion. A pounding and rubbing action is thus exerted.

The grinding effect depends then on the vertical distance of the drop, the velocity of the drum and weight and number of the pebbles.

*In figure 44 the angle, a, of the formula is indicated by the Greek letter Psi.

The velocity of the drum must be great enough so that the curvilinear motion can be well developed. Harder materials require a higher drop and heavier pebbles than softer, and steel balls can hence do the same work in smaller mills as flint pebbles in larger ones. The greater the number of pebbles, the greater is, of course, the grinding effect. It was also found that the exit of the material being ground was at a much higher point than the inlet, and hence it is not necessary to incline the axis of the mill toward the discharge end.

What causes the material to forward is now the question. As the pebbles descend from their highest point and strike the material to be ground the latter is splashed quite a distance, and if there is much material present a good deal will thus be distributed, while places where there is little throw off but a small amount. In this manner the material is distributed uniformly. This equalization takes place rapidly, as the velocity of the pebbles is quite great, being often as great as the circumferential velocity of the mill. At the exit the ground material is thrown out through the grating, while the pebbles are retained.

The pebbles naturally wear, more or less rapidly according to the conditions under which they work. The statement was made by a builder of cement machinery that one pound of pebbles is used up for 30 barrels of cement clinker. This is certainly too small a figure. The writer was told by others that the cost of pebbles is ½ cent per barrel.

In regard to the capacity of the tube-mill, it can be said that for grinding raw stock it frequently shows a capacity of 6 tons per hour, the size of the mill being 22 feet by 5 feet. For grinding cement this machine has a capacity of from 14 to 20 barrels per hour. The power consumed is 70 to 75 horsepower, though to start the mill a momentary power of about 120 horsepower is necessary. An actual test with five tube-mills, 22 feet by 5 feet, showed a power consumption of 333 horsepower, making 66.6 horsepower for each mill.

The Griffin Mill.—The Griffin mill, shown in figure 45, consists essentially in a horizontal driving pulley (17) from which the shaft (1) is suspended by means of a universal bearing (9). To the lower extremity of the shaft the crushing roll (31) is secured, which is thus free to swing in any direction within the case. The latter consists of the base or pan (24) containing the ring, or die (70), against which the roll works and upon the inner surface of which the pulverizing is done. In dry pulverizing this pan has a number of openings through it downward, outside of the ring, which lead into a receptacle from which the material is taken by a conveyor.

Upon this base the screen (44) is secured which is surrounded with a sheet iron cover (45) and which is not used in wet grinding.

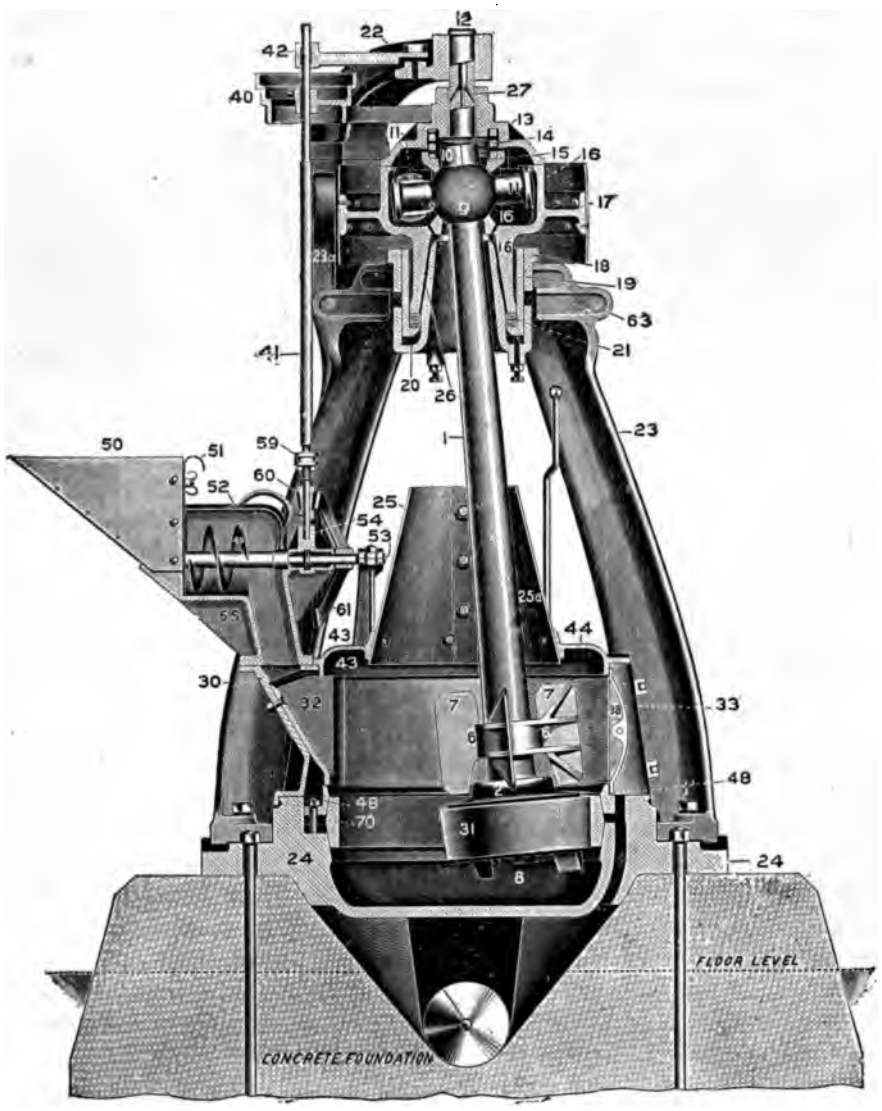

Fig. 45. Griffin mill, cross-section.

To the top of this a conical shield (25) is fastened open at the apex through which the shaft works. Just above the roll is the fan (17) which is used in the dry mill, but not in the wet. On the under side of the roll are shown shoes or plows (5) which are used in both and vary in shape according to the work to be done.

The roll is revolved within the die in the same direction that the shaft is driven, but when coming in contact with the die it travels around the die in the opposite direction from that in which the roll is revolving

with the shaft, thus giving the mill two direct actions on the material to be ground. A pressure of 6,000 pounds is brought to bear on the material to be pulverized between the roll and the die.

When a quantity of the material is fed into the mill, filling the pan as high as the shoes, on the lower side of the roll, they stir it up and throw it against the ring so that it is acted upon by the roll and crushed. All that is sufficiently fine passes at once through the screen, the coarser portion falling down to be acted upon again. The fan attached to the shaft above the roll draws air in at the top of the cone, forcing it through the screens and out into the discharge. A 16-mesh screen delivers a product of which over 90 per cent. will pass a 60-mesh screen.

The roll weighs about 100 pounds and has a diameter of 18 inches. The mill makes 200 revolutions per minute and produces about 3,500 pounds of ground clinker per hour and probably 5,000 pounds of raw stock, consuming 25 to 27 horsepower. Mechanically the machine is very efficient in its action, but being unbalanced, it requires a heavy foundation. Its drawbacks are:

1. A tendency to segregation of the raw stock owing to its centrifugal action.

2. Heavy repair expenses.

Of two particles of the same specific gravity, but of different diameters subjected to centrifugal force the larger one will move toward the circumference more rapidly; of two particles of different specific gravity, but of the same diameter, the heavier one will also move outward more rapidly. On the other hand, in a current of air of uniform velocity the larger and heavier particles will not be carried as far as the smaller and lighter ones. If now in the Griffin mill the force tending to separate the particles by throwing the larger particles farther outward were equal to the force produced by the fan, which carries the finer particles farther, no segregation would take place. Just in how far these forces are balanced in this mill the writer does not know, but it seems that the centrifugal force predominates. The fans also give motion to the particles by impact. It may be that this difference is of no practical importance, but it must stand as being reasonable until contradicted by definite data. It appears, hence, that in a mixture of limestone and clay the lighter clay would be blown away from the stone, while in a mixture of cement rock and limestone of about the same specific gravity no appreciable separation should take place. It must be remembered that a further separating action holds true in the space beneath the pan when the particles drop by gravity into the receiving trough. In this respect the action of the tube-mill seems to be superior to that

of the Griffin mill, though this objection does not hold for a homogeneous material like clinker. The screw conveyor beneath the Griffin mill, to be sure, does some mixing, but it may be doubted whether it does enough of it.

It is also a fact that but few cement mills employ Griffin mills for raw grinding.

The repair expenses of the Griffin mill are said to be higher than those of the tube-mill, although this difference is balanced again by the greater mechanical efficiency of the Griffin mill, which requires less power than the tube mill, the ratio per unit of cement produced being roughly, as 5:7 in favor of the Griffin mill.

HANDLING DEVICES.

In the handling of materials by the dry process horizontally and vertically the following devices may be used:

A. Conveyors.

1. Belt conveyors.
2. Scraping conveyor.
3. Pan, plate and bucket conveyors.
4. Screw conveyor.
5. Jerking troughs.
6. Cars.

B. Elevators.

1. Bucket belt conveyor.
2. Bucket chain conveyor.

Belt Conveyors.—Belt conveyors are used more commonly than other conveyors for longer distances. It is important that they be of good material and first cost should not be made an object in their selection. For carrying crushed or ground material the belt is given a trough-like shape by conical rollers or two rollers inclining towards the middle, the latter being the better way, throwing less wear on the belt. It is better to apply the power at the delivery end than at the receiving end, and the end bearings should be adjusted so as to take up the slack of the belt. These belts work satisfactorily for lengths as great as 500 feet and are the most reliable conveyors; average capacity about 10 tons per hour. They consume but little power for the work done.

Scraping Conveyors.—The scraping conveyor consists of a set of scrapers attached to an endless rope running in a steel-lined trough. This conveyor works satisfactorily only if the sheave-driving pulleys are large in diameter and the rope is run not too rapidly. It takes, however, a great deal of power and is noisy. Chains in place of the rope are much less satisfactory.

Pan or Plate Conveyors.—Pan or plate conveyors consist of steel pans fastened to link belts. These pans may have rollers attached to them which run on a track, the pans moving along between the two rails, or the pans run over fixed rollers. Usually the pans overlap each other so as to avoid spilling the material. The link belt runs over a polygonal sprocket wheel at the ends.

The bucket conveyor consists of a series of buckets suspended from two parallel link belts or from a rope, and which are fed from a bin either automatically, or, if the buckets are large, by a man who works the discharge gate of the bin. The buckets are dumped automatically by a tripper and also right themselves automatically. These conveyors are cheap to maintain and, though periodic in operation, have very large capacities.

Screw Conveyors.—Screw conveyors should in all cases be built of strong material and should not be more than 30 feet long. Their great advantage is the mixing they do. As a conveyor for short lengths they are very reliable if built strong. The consumption of power is very high for the work performed.

Jerking Conveyor.—The jerking or Kreise conveying trough consists of a trough or pipe sloping slightly downward and is given a rapid reciprocal motion, longitudinally, by a disk crank which jerks the material forward, about 350 strokes per minute, with a stroke of 1¼ inches. Such a machine, 45 feet long, requiring 2 horsepower, moves about 8 tons per hour. They may be built up to 150 feet long.

For continuous operation the belt conveyor has proven the most satisfactory in handling large quantities.

Cars.—Cars may be used for conveying larger quantities of raw stock, especially from the storage bins to the weighing platform. These are invariably moved by hand and hence the track should be so arranged that it slopes slightly in the direction in which the loaded car is to go. It is always essential that the bins have a decided slope or feed into a conical base from which the material is discharged by gravity into the cars.

Elevators.—Bucket elevators are practically the only means of conveying ground material in the vertical direction. We distinguish two kinds, belt and chain elevators. In the former the buckets are bolted to belts, in the latter they are fastened to chains. Belt elevators can be used for greater velocities than the link belt elevators, which, if run too rapidly, give constant trouble. It should always be made an object to build elevators as nearly vertical as possible, since, when inclined, they are certain to drag and wear rapidly. The elevator boots should be made easily accessible and be perfectly drained. Any dampness is certain to clog and choke up an elevator, especially after standing.

WET GRINDING.

In working wet marls two methods can be pursued. They may be worked in the wet state entirely or dried in rotary dryers and worked like a limestone mixture. The first way is usually followed for several reasons, which are viz.:

1. The mixtures are blended more easily in the wet way.

2. No elevators and conveyors are necessary in handling the raw mixture.

3. There is no expense for fuel outside of the kiln and no dryer to look after.

4. The waste heat which otherwise would escape into the kiln stack is utilized right in the kiln, expelling the water, and though the capacity of the kiln is decreased the process is simplified and no more fuel is used than if the marl were dried. The waste gases, the great source of loss in all rotary kilns, leave at a low temperature.

This applies, of course, only to materials which are dredged wet and naturally contain a large amount of water. It is obvious that the total fuel consumption per barrel is bound to be greater than it would be for dry material owing to the large amount of water present. The wet method has also to contend with difficulties arising from the "ringing" of the kilns, and requires additional power for running the agitators in the vat.

5. The wet process enables the manufacturer to be absolutely sure of his composition by the use of unit tanks and correction vats. The marls are as a rule fine grained materials, and hence no intermediate reduction machinery is necessary. The marl is charged into a wet pan or simply an agitator and mixed with sufficient water to make the desired slurry. Any stones and roots are removed here. The slurry is now pumped by means of piston or centrifugal pumps or, still better, compressed air to a coarse vibratory sieve, which removes any fibrous matter still remaining, and from there runs into a small tank kept agitated thoroughly. At the bottom of this tank a small pug-mill-like mixer is located, above which is a platform carrying the scale by means of which the clay is weighed out. To a certain volume of slurry a given weight of clay is added. This must be dry and pulverized by a disintegrator. From the mixer the combined marl and clay is pumped or run by gravity to the tube-mills. Though the marl may appear fine grained the grinding should not be slighted, since the clay frequently needs to have a most thorough disintegration. Another point to be considered is the presence of the shells so often found in marls. These, being thin and flakelike, are extremely difficult to reduce, and unless disintegrated will form troublesome particles of free lime in the cement which may give considerable annoyance, as the writer has had occasion to observe.

Usually tube-mills 18 feet by 5 feet are employed, although with marls full of shells a 22 foot mill would be none too large. Extreme care should be taken to feed the slurry at a uniform and constant rate, as otherwise all benefits of grinding are thrown away. With fine grained material the capacity of a tube-mill is quite large. At one plant with which the writer is familiar 88 cubic yards of slurry, one cubic yard being equal to from 1¾ to 2 barrels of cement, were ground by an 18 by 5 mill in 3 hours and 15 minutes, using 42 horsepower. The slurry left a residue of 4 per cent. on the hundred mesh sieve. It is important to make frequent sieve tests so as to control the grinding closely.

From the mills the slurry is pumped to large tanks holding about 80 cubic yards. These are kept agitated by means of revolving gates, screw propellers or compressed air. The first are the most wasteful of power, while the second are much more efficient. There should be three propellers, one near the bottom, one in the middle and one near the top. The lowest and the middle propeller should work upward, the top one downward. Compressed air at a pressure of from 40 to 60 pounds is said to be the cheapest mode of agitation.

There are two auxiliary tanks which do not contain the regular charge: one holds a slurry high in clay, the other high in lime. If now the slurry in one of the large tanks is found on analysis to be lacking in lime or containing an excess of it, some of the high clay or high lime correction slurry is pumped into the tank, so that after an hour's agitation the corrected slurry is ready for the kiln and the chemist is absolutely sure of his composition. By knowing the volume of the slurry in the regular tank, its composition and the amount of water it contains, and the same facts in regard to the correction slurry, the volume to be added is readily determined. By means of correction tables the amount can be read off at once. No other method of preparation offers such a complete control of the composition. From the storage tanks, the slurry is either fed through a pipe, by gravity, to the kiln, or it is allowed to flow into a pit kept agitated, from which it is pumped by means of a piston pump with adjustable stroke into the rotary.

GENERAL CONSIDERATIONS OF GRINDING.

There is a general tendency to simplify and cheapen the grinding process by the adoption of simpler and less power-consuming machines, like the rolls, and to effect the separation of the coarse particles by means of centrifugal separators or air blasts. This was carried out at the works of the Edison Portland Cement Co., New Village, N. J., on a most elaborate scale. No grinding machines are used but rolls and the fine material is removed by means of an air blast, all the coarser particles being returned to the rolls. It is readily seen that this

must result in a cheap process. But we find that this company uses as raw material a cement rock and limestone whose specific gravities are very close, and it is extremely doubtful whether their process would work with a limestone and soft clay, though it might be applied to a limestone-shale mixture provided their specific gravities were sufficiently alike, and even in this case serious doubts arise. With a cement-rock limestone mixture we have as a base a material already quite close to the Portland cement composition with all of the clay base incorporated with most of the lime. Even if some segregation took place, the resulting mixture, especially when worked and blended, cannot be far from the required composition.

Such a system could be used more generally if apparatus for intimate blending were invented, but so far no machine doing successful and cheap dry mixing has been devised, except for small quantities. There is some hope in this direction by the further application of pneumatic principles, using a differentiation of air blasts.

In the grinding of the raw mixtures it is important to establish the proper rate of feeding and time of grinding by determining the insoluble residue on ignition as described in the chapter on chemical examination. Practically no insoluble residue should be left. In this manner we cannot only see that the mixture is intimate enough, but also that the grinding is not excessive, using more power than is necessary.

In working coarse silicious clays or a clay base of soft clay and sandstone or sand good results cannot be obtained by grinding the complete mixture with the limestone in one and the same tube-mill, unless more tube-mills are installed and the feed decreased. It would seem the best policy in this case to grind the clays separately in a tube-mill for two reasons: first, to avoid the long grinding of the entire large mass, of which the limestone being the largest component is, as a rule, not so difficult to reduce; and, secondly, because the fine particles of limestone and the fine part of the clay would continually tend to envelop the harder fragments of quartz and thus prevent their complete reduction. The clay after its preliminary grinding would then be ground and blended with the limestone in the regular tube-mills.

It has been frequently asserted by champions of the marl process that it is impossible to grind limestone and clay mixtures as fine as the marls occur in nature, and hence the product of the latter is bound to be intrinsically inferior. Also, it has been claimed that wet grinding will produce finer products than dry grinding, and that even the shapes of the quartz grains will be different when ground wet than when ground dry.

In order to examine the relative fineness of the different raw mixtures, the writer undertook the mechanical analysis of a number of samples taken from various machines used in mills visited by him. The analysis was made by the suspension method already described.

Number.	Materials used.	Fine grinding machine used.	Residue on 80 mesh sieve.	Residue on 120 mesh sieve.	Residue on 200 mesh sieve.	Grains average diameter 0.00210 in.	Grains average diameter 0.00088 in.	Grains average diameter 0.000435 in.	Finer than last size.	Total amount finer than 200 mesh.	Remarks.
			per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	
1	Limestone and shale.....	Emery mills.	2.00	8.89	4.85	16.93	8.96	8.70	48.68	83.27	Ground dry.
2	Cement rock and limestone.....	Griffin mills..	16.38	11.57	4.75	16.21	13.29	7.61	30.17	67.28	Ground dry.
3	Limestone and lay	Tube mill. ..	3.03	7.42	3.68	23.77	17.52	10.26	34.33	85.88	Ground dry.
4	Limestone and clay.....	Tube mill. ..	7.40	9.56	2.48	17.72	8.96	8.83	45.05	80.56	Ground wet.
5	Marl and clay.....	Tube mill. ..	3.04	5.50	5.21	21.31	12.63	9.61	44.72	87.27	Ground wet.
6	Marl and clay.....	Tube mill. ..	30.46	4.28	2.17	6.73	10.61	9.31	36.44	63.09	Ground wet.
7	Marl and clay	Tube mill. ..	2.48	5.23	2.47	16.14	14.22	12.01	47.46	89.83	Ground wet.
8	Marl and clay.....	Tube mill. ..	26.74	6.99	2.13	10.52	9.77	7.67	36.18	64.14	Shells in marl quite evident.

It is thus seen that in these raw mixtures there is practically no difference in the fineness attained in grinding between limestone-clay and marl mixes. The figures of the analysis themselves are of interest inasmuch as they show how far the fineness is really carried in practical work. The last column of figures showing the amount of matter finer than 200 mesh is the best gauge of the fineness.

The question of the grinding of quartz being an interesting one from the practical standpoint, it seemed worth while to the writer to determine on a small scale, if possible, how far the grinding of quartz has progressed during a certain period of time during which the same weight of a limestone clay mixture has been ground to the desired fineness, passing through a 100-mesh sieve and leaving no residue after ignition and treatment with hydrochloric acid and sodium carbonate solutions. This work was carried out by taking 25 pounds of a raw cement mixture consisting of Wellston limestone and silicious clay obtained from a drift deposit on the State University campus passing a 10-mesh sieve and grinding the mixture in an iron ball-mill with 136 pounds of flint pebbles till it answered the above tests, which required four hours. This time could thus be taken as representing the time necessary for the thorough grinding of a commercial cement mixture.

A charge of 25 pounds of glass sand whose mechanical analysis was as given below was placed in the mill with 136 pounds of pebbles and ground somewhat over four hours.

	Per cents.
Residue on 40 mesh sieve	49.16
Residue on 60 mesh sieve	33.26
Residue on 80 mesh sieve	6.82
Residue on 100 mesh sieve	6.64
Residue on 120 mesh sieve	1.77
Residue on 150 mesh sieve	1.03
Residue on 200 mesh sieve	0.29
Finer than 200 mesh sieve	0.54

There was only 0.83 per cent. of chemically available material in this sand. At intervals of 15 and toward the end of 30 minutes the mill was stopped and a small sample removed for mechanical analysis. This was carried out as described in Chapter III. Everything passing the 150 mesh sieve was called chemically available, as previous experiments had shown that quartz of this fineness was rendered soluble in acid and alkali by ignition with lime.

The results of these experiments are shown by the accompanying curve, figure, 46, in which we find that in 250 minutes the sand contained 82½ per cent. of chemically available material. This means, therefore, that in the time required to grind 25 pounds of a limestone clay mixture sufficiently fine, the same amount of quartz sand ground under the same conditions (27 revolutions per minute of the mill already described elsewhere) had but 0.8 of the quartz chemically available.

CURVES SHOWING PROCESS OF GRINDING QUARTZ SAND IN A DRY BALL MILL.
136 LB. FLINT PEBBLE, 25 LB. OF QUARTZ.

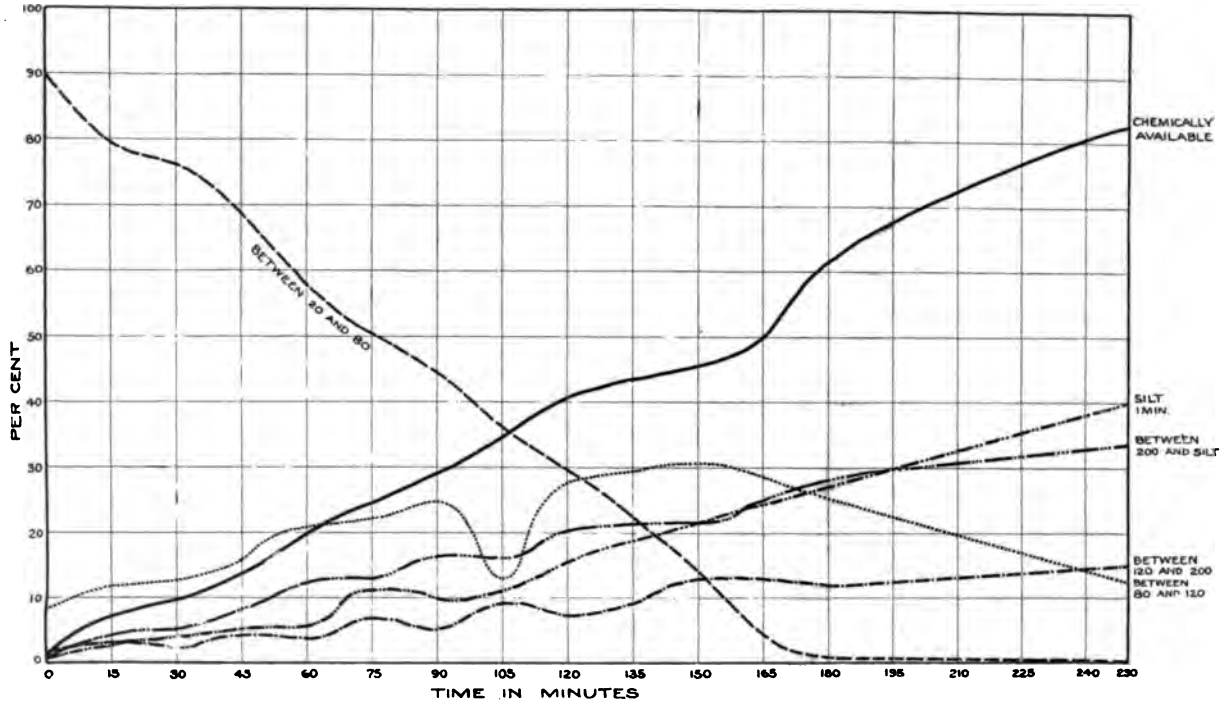

Fig. 46. Curve, showing rate of reduction of quartz in fine grinding.

This tends to show that it is possible to grind sand or sandstone sufficiently fine for cement purposes, if either more time is allowed for the grinding or it is carried on separately. It will be noticed that the curve of "chemically available" material does not change materially in its slope, which seems to indicate that in 5-4 the time, that is, in about 310 minutes, practically all of the quartz would have been rendered chemically available. The most important fact brought out by this experiment is this uniform slope, for if the output of really fine material were to decrease as the grinding, that is, the bulk of fine particles increases, the feasibility of the fine grinding would seem more or less problematical. It was intended to carry out the experiment with coarse quartz sand, clay and limestone mixtures, but the breaking of the mill due to unusually severe work put a stop to the experiments.

CHAPTER VIII.

THE BURNING OF PORTLAND CEMENT—THE GRINDING OF THE CLINKER AND GENERAL ARRANGEMENT OF PLANTS.

The raw mixture, fine ground, is now ready for burning, which is done, in American practice, almost exclusively in the rotary kiln, since this is by far the most economical and efficient apparatus for this purpose, in spite of its high fuel consumption. It consists essentially of a long tube of sheet steel, about 7-16 inch thick, usually 60 feet long and six feet in diameter, which is lined with fire brick forming a layer decreasing from 9 down to 4 inches in thickness. The tube is provided with two flanges 5 inches wide, one 9 feet from the lower end, the other about 11 feet from the upper end, each running on two pairs of cast steel wheels, 22 inches in diameter and 6 inches face, which are apart a distance of 46 inches from center to center.

The kiln is rotated by means of a cast iron or steel gearing about 24 feet from the upper end, which is provided with expansion leaves, is 74 inches in diameter, has a 6 inch face, 3 inch pitch and 75 teeth and consists of two parts. At the lower end is located a heavily bricked head supported by four cast iron wheels which vary from 1 to 2 feet in diameter and which enable the head to be moved away from the kiln. The shell is riveted flat on the inside, the rivets being ¾ inch and spaced 4 inches from center to center. The lining consists of the best grade of firebricks in the hottest zone of the kiln and the so-called blast furnace grade in the cooler portion. The stack is from 60 to 80 feet high, and 3 to 4 feet in diameter; the lower forty feet consist of 3-16 inch sheet steel, the remaining part of ⅛ inch sheet steel with 7-16 inch rivets.

According to the different requirements of different plants, the kiln is revolved slower or faster, the average velocity being about one revolution per minute. The slope of the kiln is about 3 feet in 60 feet. By means of a single pipe, powdered coal dust is blown into the kiln, the blast being furnished by a fan blower. The ground mixture is introduced either through a pipe, if slurry, or by means of a screw conveyor, if dry.

The kilns are sometimes arranged with a tapered receiving end for dry materials. The kiln is also provided with a speed regulator, of which there are several types on the market.

Fig. 47. Rotary kiln as constructed by the Allis-Chalmers Co.

The illustration on page 289 shows a modern rotary kiln as erected by the Allis Chalmers Company.

The burning process proper is extremely simple. A fire is started with wood and as soon as this is burning briskly coal dust is blown in, in gradually larger quantities till the desired heat is being produced. The

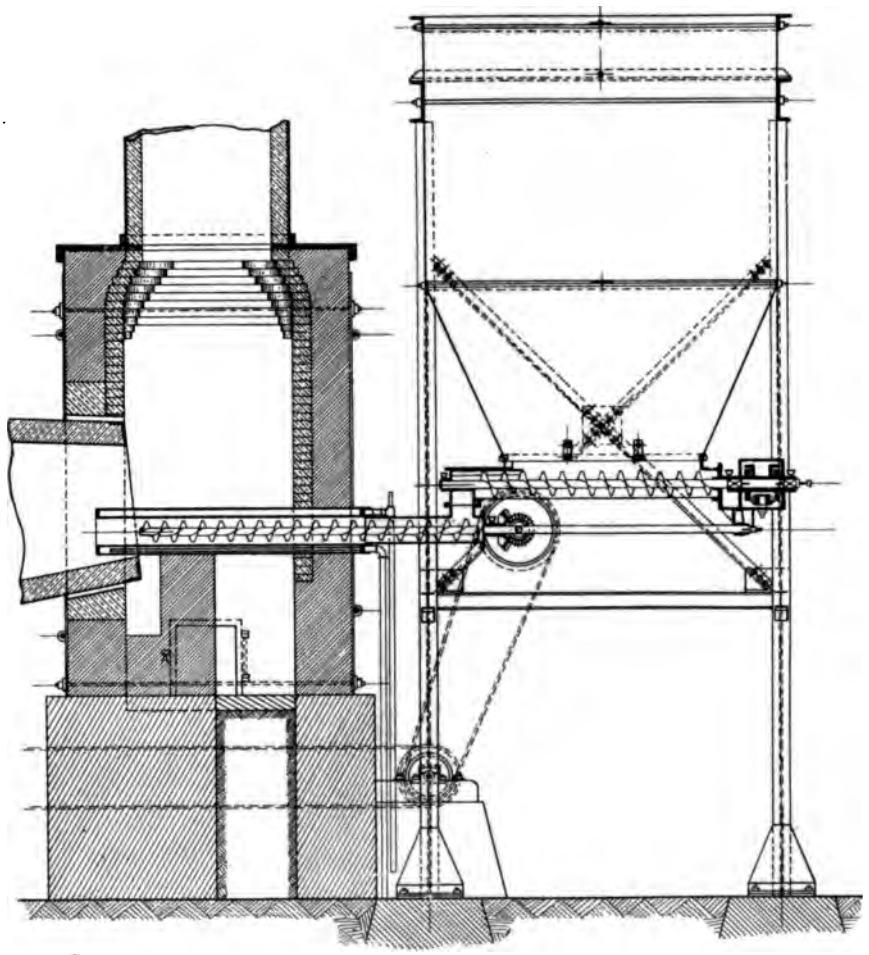

Fig. 48. Diagram, showing method of feeding a rotary kiln, with dry powdered cement batch.

cement mixture is then fed to the kiln in a regular supply and the burning thus begun, which is kept up for six days in the week until the lining shows signs of giving way. The clinker, in the shape of black roundish balls from the size of a pea up to that of a walnut, often consisting of aggregates which cling together in clusters, is discharged in a regular stream. The air required for combustion enters partly with

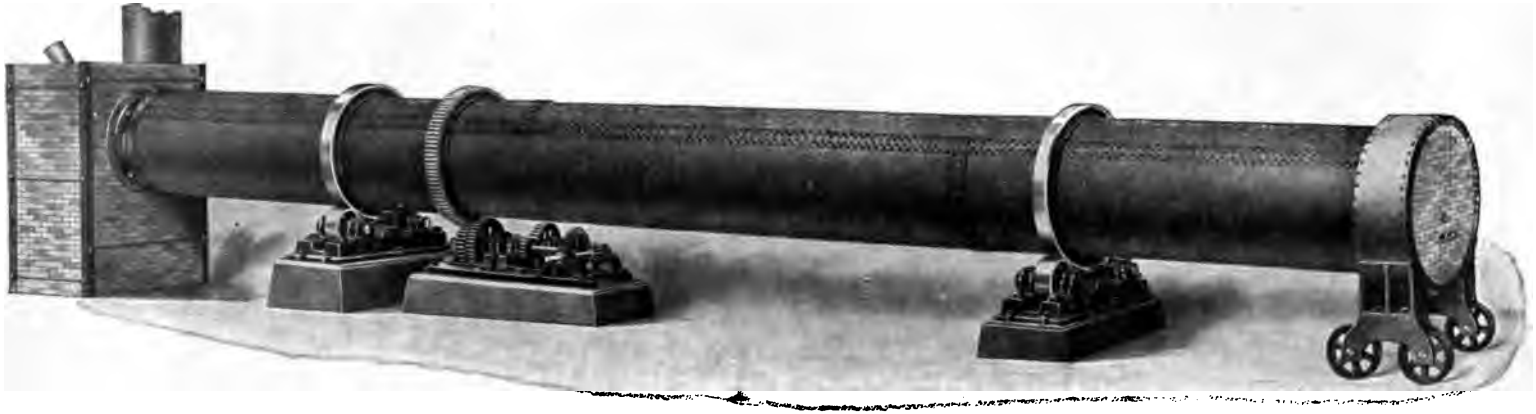

Fig. 49. Rotary cement kiln, as constructed by the Bonnot Co., Canton, Ohio.

the blast carrying the coal dust, partly through air supply doors in the kiln head and partly through the opening through which the clinker is discharged. Its supply is solely gauged by the appearance of the clinker, that is, as much or as little air is used as will produce the right kind of clinker, irrespective of the coal consumption. The burner has as many as three means of regulation available for controlling the burning process, namely, the speed of the kiln, the rate of feeding the mixture and the rate of feeding the coal dust. In some plants the mixture feed cannot be regulated so as to insure a steadier output, thus compelling the burner to work up to a definite adjustment. This seems more satisfactory, as with three means of regulation an indifferent burner is liable to become confused and does not do justice to the kiln, though it cannot be denied that in the hands of an expert burner the best results are obtained with three means of regulation. With a rapid cement feed the burner, on the other hand, desires to be on the safe side by using plenty of coal, thus tending to use more fuel than is necessary. The proper temperature is gauged by the appearance of the clinker as it passes down the kiln.

Two means of adjustment have so far not been made use of to any extent, namely, the regulation of the blast pressure and of the direction of the coal dust blast into the kiln.

The first means imply the use of a higher pressure, which can be cut down as desired, or the use of a coal blast pipe with a steady pressure and an auxiliary air pipe which may be regulated to suit the various conditions. At the works of the Edison Portland Cement Co., high air pressure is employed, as high as 60 pounds to the square inch, the writer was informed.

The second method of bringing in the auxiliary air has been strongly recommended by several cement men. In this case an air chamber is built into the head from which the air flows upward, impinging upon the stream of coal dust at an angle and thus increasing the volume of the flame from a narrow to a larger zone.

In regard to the direction of the coal dust blast Dr. Valeur reports some interesting observations. In a kiln rotating in the direction of the hands of a clock the clinker rises on the wall of the left side of the kiln while the right side is practically bare. The blast was introduced at the left side of the kiln and assumed a rotary or gyratory motion. After striking the bare wall of the right side of the kiln it again returned to the left side. At the place where the flame strikes the bare wall of the kiln it softens the brick which, hence, when coming in contact with the clinker, are worn by abrasion and succumb very rapidly. This experience caused Dr. Valeur to adjust the angle of the blast so that it struck the left side of the kiln at a definite distance, 4½ feet from the end, with

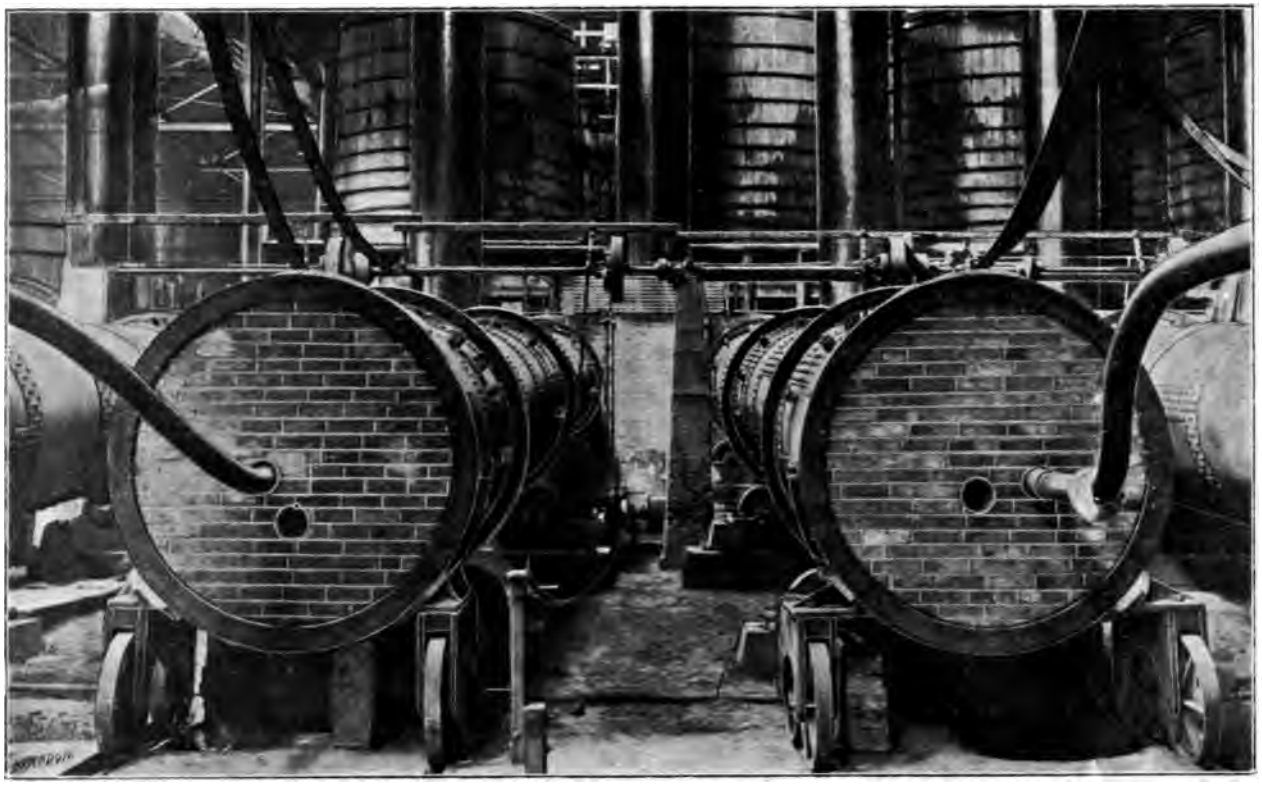

Fig. 50. View of two rotary kilns, at the furnace end, showing the pipes through which the fuel is supplied.

which the flame was not deflected at all, but followed the left side of the kiln throughout. In this manner he succeeded in increasing the output from 140 to 200 barrels per day and the coal consumption was lowered from 138 to 110 pounds per barrel. The saving in kiln repairs also was quite striking, it being reduced to two repairs per year. Likewise the

Fig. 51. View along the side of a rotary kiln, showing the coal-dust storage tank, and pipe through which the dust is being blown into the furnace. The cement-batch tanks in the distance at the other end of the kiln.

formation of rings, the wet method being used, was reduced to a minimum, so that the kiln could be operated for two weeks without stoppage on this account.

Coal Used.—The kind of coal used is of great importance inasmuch as it must contain the proper amount of volatile combustible matter in order to ignite quickly, at the proper distance, so that the maximum temperature is produced at the right point, about 10½ feet from the lower

end of the kiln. If a coal is used which ignites less readily, the ignition takes place too far up in the kiln and the zone of maximum temperature is therefore too far removed and causes ringing and other difficulties, besides making it difficult to watch the vitrification of the clinker at close range. And again, this moving back of the clinkering zone causes the waste gases to leave at a higher temperature with subsequent greater loss of heat. Probably one of the best coals used for this purpose is the Pittsburg coal of the following composition:

Ultimate Analysis.

	Per cents.
Carbon	75.24
Hydrogen	5.18
Oxygen	8.24
Nitrogen	1.51
Sulphur	1.79
Ash	8.02

Proximate Analysis.

Moisture	1.37
Volatile combustible matter	36.80
Fixed carbon	53.81
Ash	8.02

The average composition of a good West Virginia coal from Fairmont largely used for cement burning is:

Ultimate Analysis.

	Per cents.
Carbon	73.60
Hydrogen	5.30
Nitrogen	1.70
Sulphur	0.75
Oxygen	10.00
Moisture	0.60
Ash	8.05

Proximate Analysis.

Moisture	0.60
Volatile combustible matter	38.10
Fixed carbon	53.24
Ash	8.06

The chief considerations to be taken into account when selecting a cement coal are:

1. Heating power must be sufficiently high.
2. Sufficient amount of volatile combustible matter.
3. Low sulphur content not more than 2 to 2½ per cent.
4. Not more than 10 per cent. of ash.

The reasons for requirements one and two are, of course, obvious. In regard to the sulphur it must be said that it may give rise to considerable trouble if too great in amount. By keeping the fire reducing in character much of the sulphur may be carried off in the gases without absorption by the cement and in exceptionally bad cases a small amount of coal low in sulphur may be ground with the raw mixture. This, together with the reducing conditions and the high temperature, will keep out any dangerous amount of sulphur. Oxidizing burning conditions, i. e., firing with excess of air, will invariably tend to retain a great deal of the sulphur of the coal in the cement. Searching investigations in regard to the absorption of sulphur by cement in the rotary kiln have not yet been carried out.

There is no practical method for eliminating the sulphur from the coal. Even when coal is converted into gas fuel, which admits of a treatment with chemical reagents, through scrubbing apparatus, it cannot be wholly desulphurized at reasonable cost.

Since in the white hot kiln, the fine particles of coal ash are fluxed or fused into the cement and become a part of it, it is evident that its importance depends on the composition as well as on the amount. A silicious ash is bound to give rise to more serious disturbance than a basic ash. But we are able to eliminate the ash, if necessary, by gasification, a perfectly practical procedure. In this manner many coals otherwise unsuitable can be used successfully. This problem is sure to be met by some manufacturers and the use of very high-ash coals, obtained at a low cost, will thus become possible.

Producer Gas.—It has been said that fuel gas has too low a calorific power for use in the rotary kiln, but this opinion is evidently wrong for fuel gas made under proper conditions. The production of generator gas is not a process as thoroughly understood by many who operate generators as would be desirable, and hence the results are often extremely irrational. For firing a rotary kiln bituminous coal is best used in the generator. In brief, the latter consists of a circular shaft (see figure 52) provided with a flat grate and a coal charging device on top. After a fire has been built up, coal is charged till a heavy bed of ignited coal is formed with a comparatively cool zone on top. A certain amount of steam is blown in; the amount must be so regulated that not more than 800 pounds of steam is brought in for each ton of carbon. Some generators are provided with a revolving grate which ejects the ash and coal clinkers mechanically. The Taylor generator, which represents a good sample of a modern gas producer, is of this construction. The steam jet not only introduces steam, but also regulates the amount of air taken into the generator. We can distinguish three zones in the producer:

A. The ash zone.
B. The combustion zone.
C. The distillation zone.

It is important that the mass of coal be kept from fissuring, since this would tend to produce carbon dioxide, thus lowering the heating value of the gas and increasing the generator temperature. The steam is introduced for the purpose of keeping the generator temperature down, this being an extremely essential point upon which the success of the

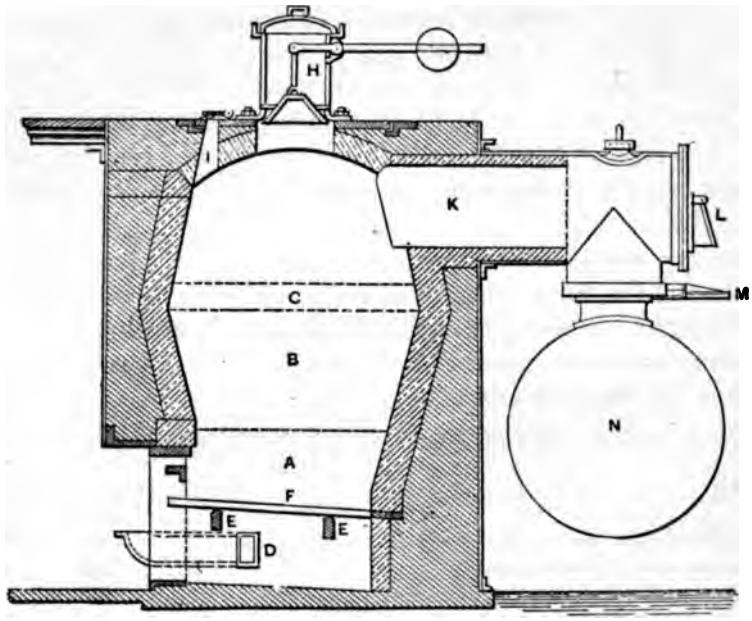

Fig. 52. Cross-section of fixed grate gas producer.

generator hinges. The steam is decomposed into oxygen and hydrogen, the gas being thus enriched by the presence of the latter gas. At the same time it is essential that not too much steam be added, or the temperature would fall too low for its decomposition and it would merely dilute the gas instead of enriching it. The following analyses represent an average composition by volume of bituminous producer gas:

	Per cents.	
Carbon monoxide	23.7	27.0
Hydrogen	8.0	12.0
Marsh gas	2.2	2.5
Carbon dioxide	4.1	2.0
Nitrogen	62.0	56.5

The calorific power of bituminous gas is on the average 2809 B. T. U. per pound or 187 B. T. U. per cubic foot. The efficiency of the conversion from the coal to the gas is claimed to be 88 per cent. The specific gravity is nearly the same as air, about 0.97. In examining the

efficiency of a producer the amount of steam in the gas should be frequently determined by absorption and weighing the condensed steam. By keeping the generator as cool and the amount of steam as small as possible, it will give no trouble as a rule. It is also of importance to have the generator sufficiently large so as to supply all of the gas needed with ease, without forcing the combustion too rapidly. It is much better to have two larger generators in place of four smaller ones. The gas should be conducted into the kilns through as short a flue as possible, so as to avoid the loss of the tarry matter which otherwise deposits. Gas firing should invariably be connected with regeneration, that is, using the waste heat of the kiln for pre-heating the air to be mixed with the producer gas. Without regeneration the system of gas firing loses much of its value.

No one should employ producer gas if it is at all possible to use suitable coal for direct firing. Gas firing can never become fully as efficient as dust coal firing, as certain losses, both chemical and mechanical are bound to occur. Some of these heat losses of a gas generator are shown in the following tabulation:

Assumed total calorific power of coal, 8,198 calories per kilogram.

	Calories.	Per cent of total heat generated.
Potential heat lost in ash or carbon	483	5.9
Latent heat of volatilization	600	7.3
Decomposition and heating of steam	356	4.3
Radiation and conduction	355	4.3
Sensible heat of gas	1,085	13.2
Total loss of heat	2,879	35.0

Some loss would occur under these same heads in direct firing, but not in as great degree, the difference being about 15 per cent. in favor of direct firing.

Ohio Coals.—It is impossible to give a discussion of the available Ohio coals in this report, a subject so admirably treated by the late Dr. Edward Orton, Sr., in his various reports of the Ohio Geological Survey. The writer will restrict himself to giving the analyses of a number of coals more especially available for cement burning.

The analyses on the following table showing the calorific powers have been obtained through the kindness of Prof. N. W. Lord in advance of his report on the constitution and chemical properties of the Ohio coals to be published by this Survey. Though some of its best coal fields have been largely exploited, Ohio still has large quantities of coal suitable for cement purposes.

Location.	Moisture.	Volatile combustible matter.	Fixed carbon.	Ash.	Sulphur.	Calorific power.
Peacock Mine, Pomeroy.....	4.75	39.15	50.35	5.75	0.77	
Minersville.....	3.50	40.17	47.89	8.14	1.96	
Syracuse.....	5.04	37.58	51.82	5.56	1.49	
Mineral, Athens Co., No. 6..	6.80	36.90	48.25	8.05	2.14	6,794
Continental Coal Co., Brenholt's No. 6.....	7.55	34.03	52.57	5.85	0.77	6,950
N. Pittsburg Coal Co., Buchtel.....	7.45	35.01	52.73	4.81	0.66	7,057
Sand Run, Hocking Co., 6...	7.40	34.17	53.43	5.00	1.06	7,027
Continental Coal Co., Gloucester, No. 6.....	7.14	34.22	51.92	6.72	1.65	6,863
Continental Coal Co., No. 6 Jacksonville.....	7.28	32.38	53.61	6.73	0.86	6,894
Corning, No. 6.....	6.79	35.45	51.85	5.91	1.00	6,903
Bird's Run, Guernsey Co. No. 6	10.93	34.00	48.43	6.64	2.03	6,133
Upson's Mine, Shawnee.....	7.76	33.50	51.27	7.47	1.45	6,772
Luhrig Mine, Athens Co....	6.17	36.40	49.61	7.82	0.90	6,868
Meigs creek coal.....	3.18	38.31	50.10	8.41	1.28	

Fuel Consumption in the Rotary Kiln.—This is a large item and it is in this respect that the rotary kiln shows to its poorest advantage.

S. B. Newberry has calculated the amount of coal required under different conditions, burning wet and dry mixtures, assuming that the cement has an average composition and requires a burning temperature of 2500° F. The coal assumed to be used is Pittsburg coal with a calorific power of 13,400 B. T. U., requiring 10.2 pounds of air per pound of coal. The calculation is based on the barrel as a unit.

Burning a dry mixture, a rotary kiln with the waste gases escaping at 1500° F., and with theoretical amount of air, requires per barrel 628,902 B. T. U. or 66.9 pounds of Pittsburg coal; with 50 per cent. air excess 82.2 pounds of coal are needed. The actual amount of coal required in practice is 110 to 120 pounds per barrel.

The rotary kiln fed with slurry containing 50 per cent. of water with gases leaving at 700° F. requires per barrel, with theoretical air supply, 120 pounds; with 50 per cent air excess, 128.7 pounds of coal. The amount of coal actually used is 150 to 160 pounds per barrel.

In these calculations the heat liberated by the chemical combination between the silica, alumina and lime has been neglected.

handling such a delicate instrument. For certain investigations, however, adjustment of coal feed or air inlet, endeavoring to fix the most favorable working conditions, these instruments in the hands of the technically trained men are valuable adjuncts. Other pyrometers, like the Chatelier, the Siemens and the air pyrometer, could hardly withstand the intense usage in the hot end of the rotary kiln due to the action of the volatilized alkali, ash, etc. The Chatelier pyrometer could be used in the upper end of the kiln for indicating the fluctuations in temperature

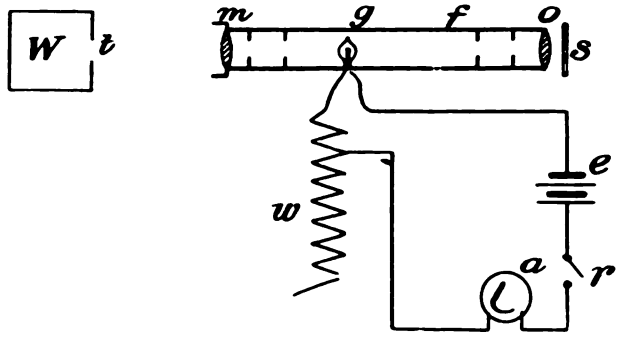

Fig. 53. Optical pyrometer, of the Wanner type.

and could be arranged to make automatic records, at the office. By means of an automatic switchboard one or two galvanometers could be made to serve an entire plant, though, of course, each kiln would require its own thermo couple. By using suitable clay shields the couple could be sufficiently protected for long usage. But, as has been said before, in the hands of untrained men all these instruments are of questionable value. For purposes of pyrometrical study the Chatelier pyrometer is preferred by the writer to any other.

REDUCTION OF HEAT LOSSES.

The *heat losses* of the rotary kiln may be reduced by the following changes:

1. Lengthening the kiln.
2. Utilizing the heat of the waste gases.
3. Utilizing the heat of the clinker.

Lengthening the Kiln.—1. This change, though greatly increasing the cost of the kiln, would bring about the most natural and greatest reduction in fuel consumption. This was fully realized by Edison when he constructed his kiln 150 feet in length. Owing to the great length of the tube the waste gases are compelled to leave it at a low temperature and hence part of the heat now wasted is rendered useful. By

proper jacketing the upper part of the kiln, the losses due to radiation could be reduced sufficiently so that the extra length of kiln would not give rise to excessive losses by radiation. In Germany rotary kilns are now in use, according to Michaelis, 90 feet long, which turn out, by the dry process, 300 barrels per day with a fuel consumption of from 60 to 75 pounds of coal per barrel, which is from 15 to 18 per cent. of the weight of the cement. The Edison kiln, 150 feet long, is 9 feet in diameter and is constructed of cast iron in place of steel and its fuel consumption probably approaches quite closely 50 pounds of coal per barrel. At the time the writer visited the Edison works, before they were in operation, a capacity of 700 barrels per day was expected from each kiln, based on extensive preliminary experiments.

From the theoretical standpoint, the lengthening of the kiln seems at present to be the most efficient and simplest method of reducing the losses of heat and probably will also be the direction in which the kiln is improved. All other expedients for utilizing the waste heat are secondary and are bound to result in a far smaller economy. If in a longer kiln, the gases are cooled to too low a temperature, mechanical draft must replace the stacks. For the wet process, however, the length of the kiln is limited by the dew point of the water-laden gases which are passing out from the kiln. Thus a 90 foot kiln having a capacity of 200 barrels per day, using a slurry containing 50 per cent. of water and consuming 120 pounds of coal per barrel, should not discharge the waste gases at a temperature below 85° C. If the temperature is lower, the kiln is too long. It has been assumed in this illustration that only the amount of air theoretically required for the combustion of the coal is introduced. Sometimes the statement is made that in burning by the wet process it is necessary to use excess of air, as the theoretical volume of air could not carry the great volume of steam evolved from the slurry. This evidently is not true; in fact, with the wet process, it is necessary to use as little air as possible in order to maintain the stack temperature high enough for sufficient draft. Taking it altogether, there is no serious complaint to make against the heat wasted in the rotary kiln fed with slurry. As long as the manufacturer starts with materials containing naturally much water and is compelled to evaporate this water, this might as well be done in the kiln as anywhere else, as long as it does not cause serious trouble there due to organic matter, forming of "rings," etc. Marl containing not more than 15 to 25 per cent of water should not be worked wet, but should be dried in the rotary dryer in the beginning of the process and then worked like any other dry mixture. Marl excessively high in organic matter likewise should be dried previous to grinding and burning. This is due to the fact that in the wet rotary,

the zone of high temperature is too short to allow of the complete combustion of the fine organic matter surrounded by the cement mixture.

The addition of water to typically dry materials like limestone and clay for the purpose of bringing about more intimate blending and more complete control of the mixture is not justified in principle.

Use of Waste Gases.—2. The idea of a long rotary kiln and the use of the waste heat has long been realized by inventors and engineers. The kiln proposed by De Navarro in 1891 employed the heat of the waste gases for preheating the air used in combustion, using also the heat of the cooling clinker. At Warners, N. Y., the waste gases were used for drying the clay and marl in a separate cylinder. The Stokes system of England does practically the same thing. Giron, in 1893, suggested the setting up of a boiler at the discharge end of the kiln, an idea which has recently again been taken up and carried out on a large scale by Prof. Carpenter of Cornell University.* A vertical water tube boiler was installed for each two kilns of a cement plant, the boiler having a heating surface of 3,000 square feet. Each boiler, however, was provided with furnaces for direct firing, if necessary. An elaborate and exhaustive boiler test developed the fact that two kilns generated 264 boiler horsepower. Another test showed that 254 horsepower were generated by the two kilns. During these tests the two kilns produced 8,018 pounds of clinker and consumed 1,888 pounds of coal per hour. The temperature, as measured by the Noel optical pyrometer, varied from 2350 to 2960° F. The gases left the boiler at 560° F., and the economizer at 350° F. During the test about 80 per cent. of the air entering the kiln was heated 480° F., restoring to the kilns 2,000,000, B. T. U. per hour, or 7 per cent. of the heat produced by the combustion of the coal. Some difficulty was experienced by the settling of kiln dust on the boiler tubes, about 4 pounds per hour, which was blown off every five hours. By the use of dust chambers as applied in blast furnace practice this slight difficulty should be entirely removed. In several other plants this difficulty is being overcome. The temperature in the burning zone of the kiln was about 2850° F.

Over one-half of the heat is discharged into the flue, of which 70 per cent. is utilized in steam, about one-sixth leaves with the clinker and about one-twelfth is lost by radiation.

Prof. Carpenter gives the following data which are very useful for purposes of reference:

*Cement, Vol. V, No. 8.

Data Obtained in Test of Two Rotary Cement Kilns, with Waste Heat Boilers.

Coal consumed per hour, lbs	1,888
Specific heat of clinker	0.2
Clinker produced per hour, (CaO=62%) lbs	8,018
Weight calcium carbonate per hour, lbs	8,875
Moisture in raw material	3.1
Weight of carbon dioxide evolved per hour, lbs	3,660
Weight of air supplied per pound of coal, at 44% excess, lbs.	16.1
Total weight of air supplied per hour, lbs	32,397
Weight of air supplied by coal feeders per hour, lbs	5,850
Total weight of gases discharged per hour, lbs	37,749
Heat discharged per pound of gas 0.23(1800–100)B.T.U.	391
Area of outside of kiln, square feet	1,213
Area of hood exposed, square feet	76
Air entering kilns, average temperature, deg. F	480
Air leaving kilns, average temperature, deg. F	1,820
Air leaving boiler, average temperature, deg. F	660
Air leaving economizer, average temperature, deg. F	450
Temperature of kiln, lower third, deg. F	2,350 to 2,960°
Temperature of kiln, upper part, deg. F	2,960 to 1,800°

Heat Distribution.	B. T. U.	Per cent.
Total heat supplied, including heat of formation of silicates	31,371,0 0	100.
Discharged from kiln to boiler	14,859,859	47.8
Discharged with clinker (8,018 x 0.2 x 500)	4,409,540	14.2
Calcium carbonate decomposed (18,875 lbs., 765 per lb.)	6,789,375	22.2
126 lbs. sulphur trioxide liberated	238,140	0.7
252 lbs. water evaporated	303,200	0.9
Radiation and uncccounted for	4,770,886	14.2
Radiation per sq. ft. of surface of kiln per hour	1,700	....
Heat absorbed by boiler from kiln gases	8,798,328	28.8
Heat absorbed by economizer	1,178,998	3.8
Stack loss and boiler radiation	4,882,533	15.6

To show the progress of the cement burning in the rotary kiln W. B. Newberry* examined the contents of a cooled, but not emptied, rotary kiln by taking samples at regular intervals of 48 inches throughout the kiln, starting with unburnt stone and finishing with the vitrified, perfect clinker within 48 inches of the lower end, 14 samples being taken. The kiln was fed with a cement rock limestone mixture and was 60 feet long,

*"*Cement and Engineering News*," 1902.

5½ feet in diameter and made one revolution in one minute and 30 seconds. Each sample was analyzed. The results are given in the accompanying table:

No.	Silica.	Alumina and iron.	Lime.	Magnesia.	Loss on ignition.	Remarks.
	Per cent	Per cent	Per cent	Per cent	Per cent	
1	13.7	6.00	42.12	1.97	35.30	
2	13.65	5.58	41.95	1.96	35.04	Bluish gray in color.
3	14.38	5.70	41.63	1.88	34.84	
4	13.55	6.30	41.98	2.12	33.46	
5	14.33	6.27	44.05	1.65	32.76	Yellowish color.
6	14.46	6.36	44.67	1.89	30.56	
7	14.90	6.55	46.19	2.30	28.38	
8	16.44	6.99	49.25	2.23	29.94	Yellow to brown, balls soft.
9	17.03	7.80	53.04	2.30	18.44	
10	17.94	8.50	56.20	2.35	13.04	Bet. 10 and 11 mass hardens.
11	18.60	9.04	59.00	2.70	8.82	Vitrified on outside.
12	18.66	9.75	62.68	2.80	4.34	Brown, partially vitrified.
13	19.90	10.76	63.38	2.83	1.08	Decided difference, nearly black.
14	20.36	10.78	63.76	2 81	0.86	Black well burnt clinker

It is thus seen that the vitrification proper must take place very rapidly, being confined to the lower 12 feet of the kiln.

Utilizing the Heat of Clinker.—3. The heat from the cooling clinker is an item which deserves some attention. In a kiln of a capacity of 200 barrels per day, the clinker leaving at a temperature of 1220° C., if cooled down to 20° C. would represent an amount of heat equal to $(380\times0.2\times1200\times200\div2.2=8,304,000$ kg. calories per day, theoretically, which is equal to 1,186 kg. of coal with a calorific power of 7,000, or 2,609 pounds of this coal. Where coal is cheap, say $1.00 per ton, as in Southeastern Ohio, where the cement company generally owns its own coal mines, the heat item is not an important factor and it is doubtful whether it would pay to install an expensive apparatus for saving any of this heat, especially since probably not more than 50 per cent. of it would be made useful. The extra cost of installment, the inconvenience of the

heaters, the extra cost for power would offset the gain. The case is different where coal is higher.

In most cement plants now the main question seems to be how to cool the clinker in the quickest manner without reference to saving the heat, and hence coolers are installed without any attempt to economy. Some of these coolers are merely iron towers with baffle plates, others are high iron cylinders which are kept filled with clinker which is discharged by gravity at the bottom, but in some cases the hot air is drawn out on top by the blowers, thus preheating part of the air. In most cases the clinker is simply heaped up in a large shed or in the open air in great piles from which the cool clinker is wheeled to conveyors taking it to the grinding machines.

There are several systems of regenerating clinker coolers, viz.:

1. Revolving cylinders.
2. Vertical cylinders.
3. Grate coolers.

Revolving Cylinders.—1. The first are cylinders arranged just beneath the rotary kiln, catching the clinker as it comes from the kiln, the connection between the kiln and cooler being made as air tight as possible. The air passes over the discharged clinker into the rotary kiln, being thus preheated. In this case it is advisable to inject the coal with air under as high a pressure as possible, so that as much as possible of the secondary preheated air be used. The inclination of the cooler may be the same as that of the kiln and it is, so to speak, a piece of the kiln broken off and lowered. Or the cooler "doubles up" beneath the rotary kiln, in which case its inclination is reversed, as in the apparatus patented by Navarro in 1891 (see figure 54).

One cooling cylinder may serve for two kilns. In operation this is the simplest and most easily operated cooler, but its heating efficiency is not very great. This can be increased, however, by putting in stirring devices, especially by projecting steps along the sides of the cylinder.

Vertical Cylinders.—2. Of the vertical clinker cooler we have as probably the best example, the Wentz cooler (see figure 55), in which air is blown through a vertical pipe perforated at intervals, from which the air is distributed through masses of clinker which gradually moves downward between alternately cup and bell-like iron baffle plates. The heated air is collected in a circular space surrounding the cylinder and is then drawn into the kiln. For successful operation the apparatus requires a higher air pressure than is usually carried by the blowers. One cooler can take care of at least two kilns.

Cooling Grates.—3. The grate cooler consists essentially of a cast iron grate or steps surrounded by a shell and a device for jarring the recep-

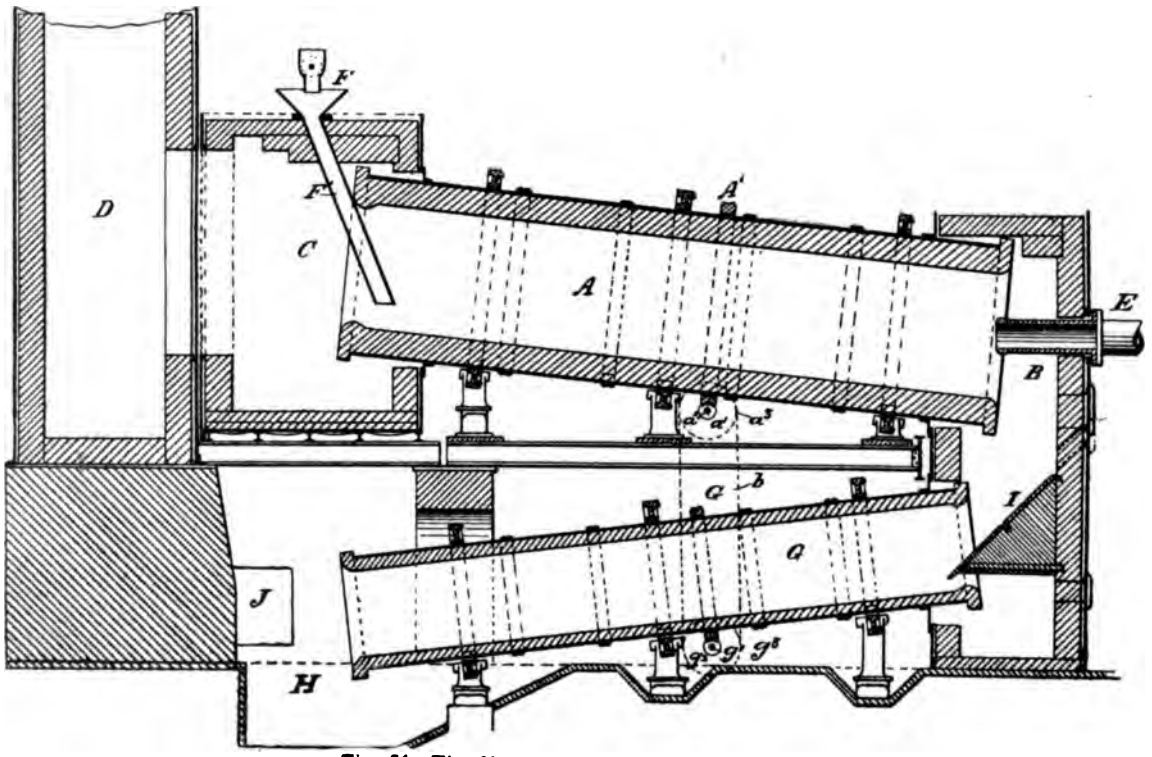

Fig. 54. The Navarro rotary clinker cooler.

tacle. The clinker drops down the grate while air enters at the inlet (see figure 55). The heated air is exhausted by means of a fan, with water jacketed bearings. This apparatus was patented by Galschioet and seems to be a compact machine which does not occupy as much space as the inclined cylinder cooler and can be fed direct from the kiln, requiring no elevator. The clinker is removed by a screw conveyor.

It would be idle to attempt to save the heat from the clinker in a dry mixture plant while no attempt is made to get back some of the much greater amount of heat lost from the short kilns. What is needed most urgently at present is the close regulation of the air inlet into the ordinary kiln. That this can be done is affirmed by Mr. H. E. Brown, chemist of the Coldwater, Mich., Portland Cement Works, who stated to the writer that the analysis of the gases in his kilns showed an air admission of 97 per cent., using the wet method. It is necessary that strict control be kept of the firing conditions in our kilns by means of the Orsat or similar apparatus.

The Edison kiln 150 feet in length solves the entire problem of fuel consumption by allowing combustion to take place some distance from the lower end. The air is thus naturally preheated by the clinker and heat radiated from the zone of combustion while the waste gases are cooled down sufficiently by the long tube and are made to preheat the mixture.

REFRACTORY KILN LINING.

The question of the kiln lining is an important and much disputed one. In the majority of cases high grade fire brick are used in the combustion zone and lower grade brick in the cooler portions of the kiln. The whole question of refractoriness hinges, first, on the chemical composition of the material, and, secondly, on its physical characteristics, size of grain and porosity. Since the lining is in contact with a basic material, we would hardly expect that a silicious lining would prove satisfactory, although the sugar industry has used for lining its limekilns quartzitic rocks with fair success. It is generally assumed that the clay substance in its ideal compositon is the best possible refractory, but we are at once confronted by the question of the kind of clay substance. We know in nature three distinct kinds of clay substances; the kaolin, forming a somewhat friable, slightly plastic mass which burns to a porous body; the horn-like, plastic ball-clay having almost the same composition, but containing small quantities of fluxes. This becomes dense even when burnt at low temperatures., but still has a high melting point; and lastly, hard non-plastic, flint clay. The kaolin is much more infusible than the ball-clay, showing a difference of perhaps 3 or 4 cones in actual melting point, but after all it does not stand up so well in the fire in contact with fluxing materials, slags or glass, simply because it is too porous in structure, allowing fused bodies to enter

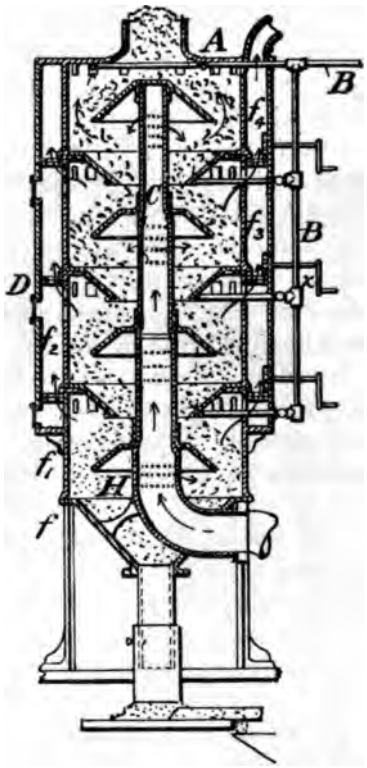

Fig. 55. The Wentz vertical clinker cooler.

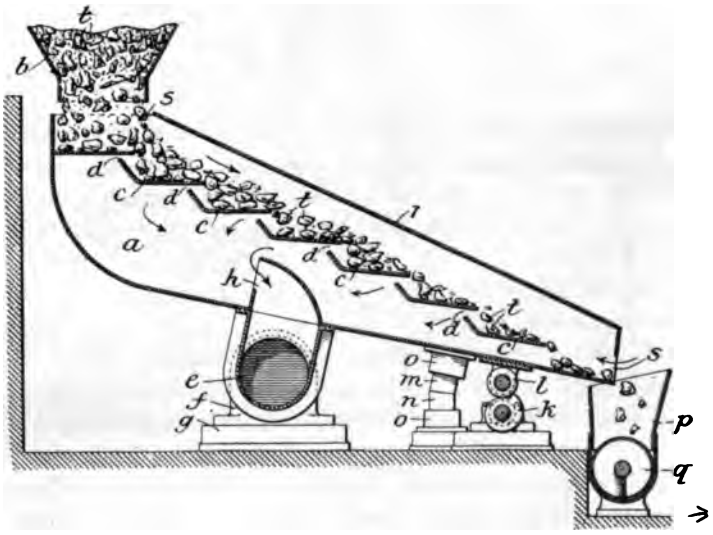

Fig. 56. The Galschioet grate cooler for cement clinker.

its pores. The third kind of clay, called flint clay, is a very hard infusible clay showing but slight plasticity, but great density. Its composition is almost identical with that of the kaolin. The latter must be ruled out owing to his porosity and we are to deal therefore with the plastic bonding clays and the flint clays. The latter, in themselves dense, would appear as the ideal refractory clay material, but there is this practical difficulty to be considered that, owing to their slight plasticity, they cannot be made into bricks by the ordinary processes. They require a certain amount of plastic clay to allow the bricks to be molded. The only method by which the amount of bond clay can be decreased is to press the bricks made from flint clay with a little plastic clay on a dry press. But this method, lacking the plastic bond developed by the use of water, results in a more or less porous brick. It might now be suggested that the flint clay be ground so coarse that its grains are difficultly attacked by the calcareous slag, but this again is not feasible, as then the bricks would become too friable and would not stand the mechanical abrasion they receive in the rotary kiln.

We are reduced, hence, to the use of a mixture of flint clay with as much plastic clay as will produce a body which is dense, but not brittle, and it is essential that the bricks are burnt as hard as possible in order that all the shrinkage may be taken out and they will not shrink in the rotary kiln. The addition of burnt clay grog to the brick mixture is not necessary unless certain shrinkage flaws show in the bricks. The sizing of the clay grains is not given the attention by fire clay men which the subject deserves. The body must not be made up of all coarse grains nor of all fine, but of a combination of both with a preponderance of the coarse grains. By coarse are meant grains between 10 and 20 mesh sieve, by fine those passing the 40 mesh.

In regard to the chemical compositon it is important to note that Seger's results require for an ideal refractory clay the composition (when burnt):

$$\left.\begin{array}{l}\text{Alumina, } 46.2\% \\ \text{Silica, } \quad 53.8\%\end{array}\right\} = Al_2O_3 2SiO_2$$

Any increase in silica above this amount will reduce the refractoriness, down to 17 equivalents of silica to one of alumina; at this point the refractoriness again begins to rise, finally reaching the fusing point of silica. Seger also expresses the comparative refractoriness of a fire clay by the formula:

$$\text{Refractory quotient} = (a+b)-\frac{a}{b}$$

where a= the molecular ratio of the alumina to the fluxes (RO), that is, equivalents of alumina divided by equivalents of fluxes (RO) and b=the molecular ratio of the silica to the fluxes.

Seger, however, makes a special point of cautioning against the neglect of the importance of the physical condition and calls attention to the

Magnesite bricks have been tried, but owing to their high price, great brittleness and high heat conducting power have not been successful.

Beauxite bricks or additions of beauxite to clay have also been disappointing as far as the writer has been able to learn.

Cement clinker linings, consisting of crushed and screened cement clinker and a little sand, have been quite successful, according to the reports of two cement mills. These linings are put in like concrete, and if they should prove satisfactory in every respect would afford an easy solution of a troublesome problem. Further data, however, are necessary before a final opinion can be given.

Kiln Improvements.—The rotary kiln is experiencing constant changes in various respects, of which a few will be quoted. Edison proposes the use of two jets of coal dust (see figure 57). Michaelis, Jr., obtained a patent on projections arranged around the kiln wall which are to retard the movement of the material downward, but which in the opinion of the writer are liable to give a great deal of trouble in operation. Another inventor proposes the uses of a water jacketed kiln lining in the hottest zone analogous to the blast furnace lining. Lessing provides the kiln with a ribbed lining through which small jets of air are forced under pressure, and a good many other modifications might be cited.

Shaft Kiln.—The vertical shaft kiln used so extensively in Europe has no place under American conditions owing to its greater cost of operation due to the extra labor required, the cost of briquetting and the irregularity in output and quality of clinker. Its intrinsic fuel consumption is, of course, considerably less than that of the rotary kiln, being about 61 pounds of coal per barrel under favorable conditions. If used at all the system adopted should include the dry pressing of the raw cement bricks and burning the kiln with forced draft so as to increase the capacity. Figure 58 represents the Dietzsch shaft kiln operated continuously.

Fusing Portland Cement.—Occasionally the idea of doing away with all intermediate and fine raw grinding machines by fusing the cement to a liquid mass and grinding the resulting cooled slag crops up. This certainly is a fascinating idea and appeals to the theoretically inclined mind quite strongly. To make Portland cement by charging limestone and clay into a blast furnace and running out the liquid slag certainly seems a simple process. Jex in 1900 suggested that the lime in the Portland cement composition be lowered, as fused cement would require less lime than vitrified cement. Thus he suggests among others a cement of the following composition:

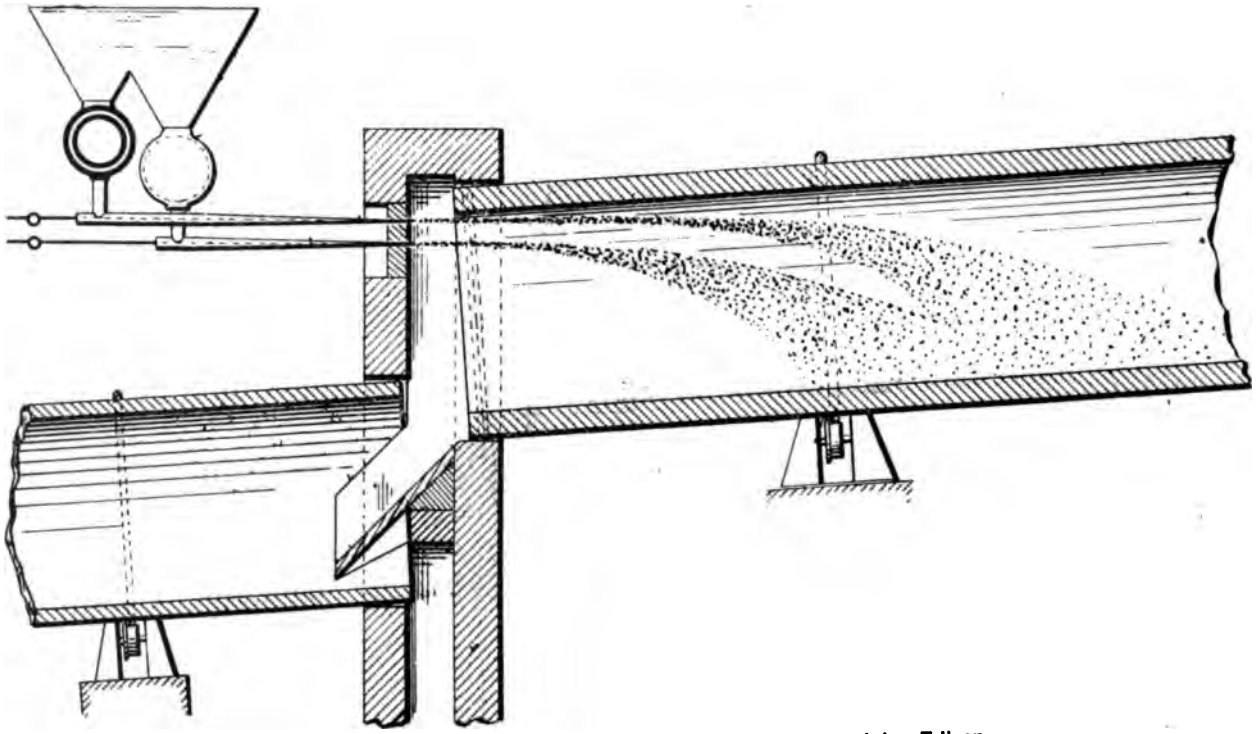

Fig. 57. The double-jet dust-coal firing system, proposed by Edison.

	Per cents.
Silica	32.55
Alumina	1.93
Ferric oxide	1.10
Calcium oxide	62.49
Magnesium oxide	1.93

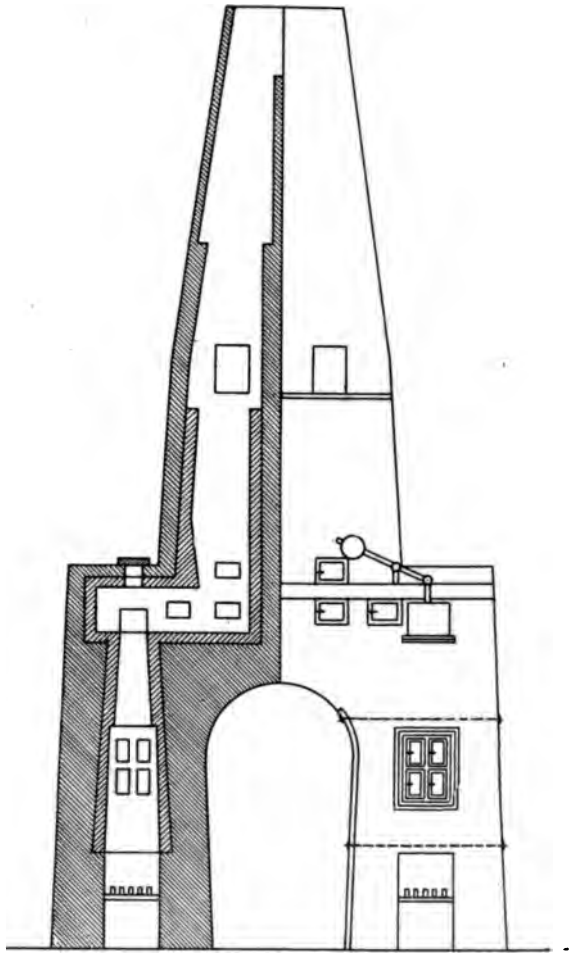

Fig. 58. The Dietzsch vertical cement kiln.

According to him the cement burnt in a shaft kiln requires 80,000 large calories per 220 pounds, while by fusion the same amount of cement could be produced with 200,000 calories, from which the heat energy corresponding to the crushing and grinding must be deducted.

Coal Grinding.—It will be found necessary quite frequently, in fact nearly always, to dry the coal in a rotary dryer before pulverizing it.

The coal is usually received in nut size. The dryer is usually about 30 feet long by 5 feet in diameter. The grinding is done in two stages. For the first grinding there may be employed:

1. Rolls.
2. Disintegrators.
3. Ball-mills.

The disintegrator appears to be the most efficient machine for this purpose. The fine grinding may be accomplished in:

1. An æro pulverizer.
2. A Griffin mill.
3. A tube mill

The æro pulverizer is a disintegrator in two or three stages, that is, with two or three revolving cages or hammers varying in size and revolving with great rapidity. The fine coal is blown up a tube and passes through a chamber in which the coarse particles are separated and drop, being returned to the pulverizer by gravity. In size the machine is much smaller than the clay or limestone disintegrators. The writer was informed by those using this machine that it is very efficient, but has a reputation, justified or not, of being somewhat dangerous owing to the great velocity of the rotating parts, and is said to be liable to coal dust explosions. This last statement, the writer has been unable to verify. This system is illustrated in Fig. 59 on page 318.

THE GRINDING OF THE CLINKER.

From the kilns, the hot clinker drops either into iron cars, a horizontal pan conveyor or a cylinder cooler. The conveyor collects the clinker from all the kilns and delivers it to a chain elevator, which again conveys it to a horizontal conveyor. The latter takes it to the clinker pile. Where vertical cylinder coolers are used, the clinker from two kilns is delivered to one cooler. In some mills the clinker is quenched by spraying water on it or the pan conveyor may be aranged to run in water so that the clinker is cooled without becoming wet. The effect of the spraying is beneficial so far as the quality of the clinker is concerned, inasmuch as clinker with any tendency to dust is improved and also it becomes more friable, easier to grind. On the other hand the heat of the clinker is thus to a large extent dissipated and it would be hardly worth while to make an attempt to save it.

The cooled clinker is now ready to be ground. At this stage the raw gypsum is added either by rough weighing or by guess, so many shovels to a barrow load of clinker. The amount usually added is 2 per cent., and the cost of the plaster is hence a considerable item in the manufacture, its cost being from 7 to 10 dollars per ton. This is a powerful argument in favor of cement compositions requiring no gypsum or but a small amount.

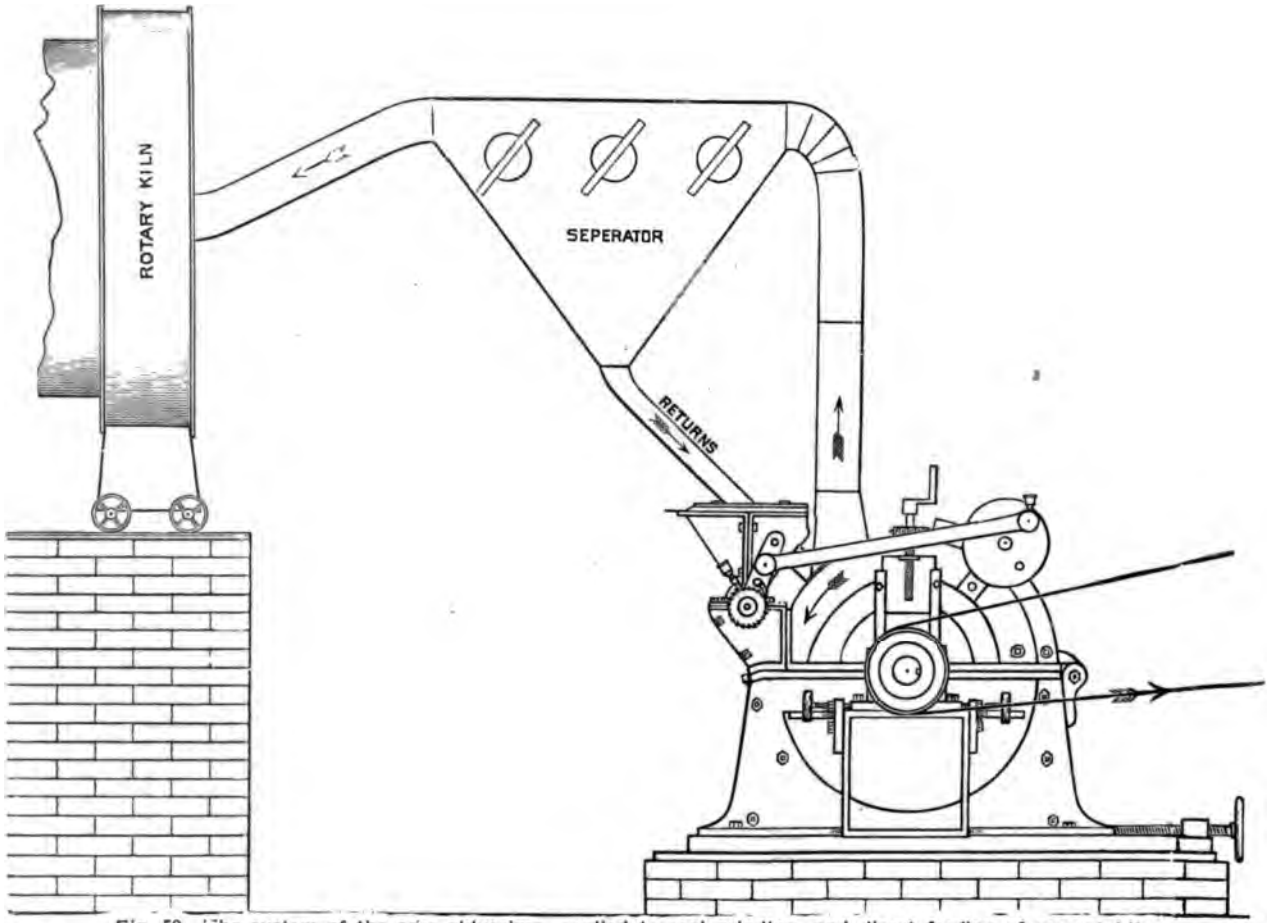

Fig. 59. The system of the aero pulverizer applied to coal grinding, and direct feeding of cement kiln.

In grinding the clinker we require again intermediate and fine grinders. The intermediate grinder may be:

1. Rolls.
2. Kent mill.
3. Disintegrator.
4. Ball-mill.

and the fine grinders:

1. Griffin mill.
2. Tube mill.

What has been said in regard to the relative mechanical efficiencies under the head of raw grinding holds true also here and the economic values of these machines range probably in the order in which they are given. One source of loss in efficiency is the fact that the fine material produced in the intermediate grinding machines passes on to the fine grinding machine and hence lessens its efficiency to this extent. This seems to the writer one defect in the usual American mechanical outfit, but can be easily remedied by the insertion of a wind separator, of which there are many makes on the market depending on centrifugal action or on simple air blasting (see figure 59). In fact these machines are probably destined to revolutionize the present clinker grinding system by doing away with the fine grinding machine entirely. This could be done by selecting a machine which furnishes a high percentage of fine material, like the Kent or ball-mill, separating out the finest by means of the wind separator and returning the coarse material to the grinding machine. This would undoubtedly cheapen the process considerably.

The clinker grinding machines according to the present system might be arranged as follows:

Rolls or Kent mill, or disintegrator, or ball-mill.
Dust separator.
Griffin or tube mill.

The rolls, with two passes, have the greatest efficiency, showing probably the least cost of power. Their capacity is about 30 tons per hour with a consumption of approximately 100 horsepower.

The Kent mill, requiring 25 to 30 horsepower, has probably an output of from 22 to 28 barels per hour, preparing the clinker for the tube mill, depending on the hardness of the clinker.

The disintegrator has been claimed by some manufacturers to be not very efficient for clinker grinding owing to the heavy expense for repairs, due to the direct impact of the rapidly revolving bars, which probably is true. The repairs for this machine in clinker grinding are considerably geater than in raw grinding, where it has proven very successful in every respect in a number of instances.

The ball-mill has been discussed sufficiently under the topic of raw grinding and was quoted as having a capacity of 12 to 16 barrels per hour through the 20 mesh sieve, requiring 30 to 40 horsepower and 18 to 24 barrels with 40 to 50 horsepower. It is not an economical machine as an intermediate grinder.

As to the comparison between the Griffin and the tube mill, it must be stated that the Griffin mill is the more economical of the two in spite of its heavy repairs. Its tendency to separate particles of different specific gravity cannot be made a point of criticism here inasmuch as the material is homogeneous in character. The capacity of a Griffin mill is from 8 to 10 barrels per hour, requiring 25 to 30 horsepower.

The capacity of the tube mill, 22 feet by 5 feet, is 14 to 20 barrels per hour, requiring 70 to 75 horsepower to operate and 125 horsepower momentarily in starting.

Fineness of Grinding.—It has been claimed repeatedly that the product of the tube mill is far higher in finest material than that of any other machine, and hence cement ground by this machine is supposed to be higher in quality owing to the large amount of cement dust present. The writer investigated this point by collecting himself samples of cement ground by several types of machines and having mechanical analyses made, using for separating the fine particles alcohol redistilled over caustic lime. The results of these analyses are shown in the following table on page 321.

These results, of course, cannot be used to condemn any machine, as other factors enter into the consideration of grinding, so that the very attempt to draw general conclusions in regard to the quality of the grinding would be absurd. However, in comparing the figures of column 10 it is seen that they are quite in favor of the Griffin mill and show that in practice this type of machine is more than the equal of the tube mill. It is also observed that the finer cements show a higher tensile strength with 1 : 3 briquettes, just as is to be expected, for the sand test is to some extent a test for fineness of grinding. There is perhaps a tendency in practice to overcrowd the tube mills or to feed them irregularly. This may account for the poorer showing of the tube mill.

These experiments, in addition, show that the usual sieve analysis is not a satisfactory and accurate means of measuring the real fineness of cement, since the 100 mesh sieve commonly employed tells practically nothing about the amount of cement dust present.

In the method proposing to use only an intermediate grinding machine, together with an air or centrifugal separator, it would probably be best to use the Kent mill or rolls. The latter have proven quite efficient at the works of the Edison Company.

Number.	Grinding machine used.	Residue on 80 mesh sieve.	Residue on 120 mesh.	Residue on 200 mesh.	Grains average diameter 0.0020 in.	Grains average diameter 0.0072 in.	Grains average diameter 0.0003 in.	Grains below last size.	Portion finer than 200 mesh.	Tensile strength 1 cement: 3 sand pounds per sq. in. after 28 days.
1	Tube mill	7.07	14.56	4.45	22.68	19.29	7.36	24.69	74.02	296
2	Tube mill	9.01	15.35	5.09	21.50	20.53	7.06	21.52	70.61	318
3	Tube mill	12.12	15.05	7.61	21.11	16.85	5.91	21.37	65.24	303
4	Tube mill	14.11	14.57	7.82	22.43	13.95	7.81	19.32	63.51	208
5	Tube mill	3.84	17.64	5.10	25.27	17.56	10.16	20.42	73.41	297
6	Griffin mill	3.06	15.41	8.24	28.56	16.48	12.74	15.51	73.29	350
7	Griffin mill	9.43	16.91	6.37	25.52	12.18	9.20	18.49	65.39	313
8	Griffin mill	5.00	15.42	14.52	27.30	19.10	9.22	14.88	70.50	285
9	Griffin mill	4.40	11.35	5.13	23.79	21.30	10.01	24.01	79.11	346
10	Griffin mill	4.18	13.30	5.07	22.63	14.64	12.31	28.79	78.37	314
11	German cement	3.88	15.84	7.63	27.63	17.83	13.30	13.89	72.65	281
12*	Mill stones	7.36	9.93	3.53	16.42	13.98	14.74	34.04	79.18	317†
13*	Mill stones	12.50	11.59	4.29	16.52	21.95	17.42	15.76	71.65	299†
14*	Tube mill	10.53	12.85	8.50	11.39	22.15	20.72	13.85	68.11	265†

*Numbers 12, 13 and 14 are Natural Cements. †1 Cement 1 sand was used in these briquettes. The tensile strengths given are the averages of five briquettes.

In regard to the capacities of the different machines Professor Carpenter gives the following summary:

Machine.	Capacity in tons per hour.	Power used.
Rock crushers		1.1 horsepower per ton.
Rolls		1.5 horsepower per ton.
Griffin mill, rock	1.5 to 3	27 to 33 horse power.
Griffin mill, clinker	0.8 to 1.5	27 to 35 horsepower.
Griffin mill, coal	1.5 to 2.0	16 to 24 horsepower.
Ball mills, on rock to 20 mesh	2 to 4	20 to 30 horsepower.
Tube mill, producing dust	2 to 4	70 to 80 horsepower.

Dust Collectors.—One class of machine found lacking in American cement mills is the dust collector of European works. Every effort is made there, made compulsory by law, to separate out the dust floating in the air as much as possible, and hence regular plants of good size are installed for this purpose. The dust being decidedly injurious to health, it should be the aim of every manufacturer to install such dust collecting plants, especially since their cost is not great and in part is repaid by the fine cement dust collected. The writer has visited plants in which the enormous amount of dust floating in the air was a positive menace to health. By the exercise of a little engineering skill this state of affairs could be remedied without difficulty, just as has been done in other industries. There are a great many appliances on the market for collecting dust by exhausting air from the working space, passing it repeatedly through settling chambers and catching the remaining particles by means of cloth filters.

MECHANICAL EQUIPMENT.

Dry Process.—We can now summarize the mechanical equipment of dry grinding cement plants as follows:

Limestone.

1. Rock crusher.
2. Intermediate grinder, (rolls, disintegrator or Kent mill).
3. Limestone Bins.

Clay or Shale.

1. Coarse grinder (rolls or rock crusher, if hard.)
2. Rotary dryer.
3. Disintegrator.
4. Clay bins.

The materials, each in separate bins, are now discharged from the bins by gravity on to horizontal belt conveyors and fed into two smaller

bins, side by side, one for the limestone and one for the clay. Here they are weighed out by means of a double scale and dumped into a large mixer of the granulator type consisting of a large box, V-shaped, in cross section, in which, at the bottom, a screw conveyor shaft revolves, carrying also larger mixing blades. The shaft is to be very heavy. The bottom of the mixer slopes from the discharge end down to the inlet end so that the space at the inlet end is far greater than at the discharge end and can be made to hold several tons of material. Being about 16 feet long, the mixer discharges the raw stock in a steady stream into a screw conveyor, not less than 8 feet long, which feeds another smaller storage bin, from which the ball-mills are supplied. This bin thus brings about additional mixing and blending. Since the material has been through an intermediate grinder before, the ball-mill has a greater capacity and its principal function is to produce further mixing and blending together with additional grinding. Two of these mills should supply four tube mills without any difficulty. Thus, starting from the separate limestone and clay bins, we have the following equipment:

a double bin,
b scales,
c mixer,
d screw conveyor,
e feeding bin,
f ball mill,
g tube mills,
h storage bin over kilns,
i rotary kilns.
j clinker cooler,
k Kent mill,
l wind separator,
m Griffin mill,
n to storage bin.

The principal advantage claimed for this arrangement is the fact that the mixture is under the best control possible in a dry plant, since storage bins are provided for, which permit of analyzing and checking the limestone and clay in bins which are independent units. Until analyzed and approved by the chemist, the bin is not to be emptied. By calculating the mixture for one limestone bin and one clay bin, which is considerably smaller, these two bins are emptied and their contents weighed out in the proportion calculated. By supplying each bin with an automatic sampling device on top its exact average composition may be obtained. Of course it is important that the bins be not too large. Such an arrangement would lessen one of the greatest objections to the dry process in which, as it is well known, errors in the com-

position cannot now be corrected in the average plants of today, but must be allowed to pass on with the certainty of producing an inferior product.

The bins, of whatever kind, should be supplied with bottoms permitting of emptying by gravity. This applies to the cement bins as well as the raw stock bins.

In the accompanying diagram this equipment is outlined. It will be noted that the draft for the kiln is provided by exhaust fans, the waste heat being passed through boilers and a feed water heater. The heat of the cooling clinker is supposed to be used for preheating the air introduced for the combustion of the coal. If the clay is very coarse, or if sandstone is added to the mixture, it might be necessary to insert a tube mill between the clay disintegrator and the clay bins, in order to insure sufficient grinding or, if preferred, another tube-mill might be added to the fine grinding equipment and the feed reduced for each mill, so that more time is given for the grinding. A flue is also indicated through which some of the waste gases might be exhausted and conducted through the dryer, so that the fuel item for the drying is eliminated. The coal should be ground in a disintegrator and Griffin mills. This diagram, of course, is only intended as a suggestion, for covering the ordinary difficulties which arise. In any individual case, modifications would be likely to be needed to suit the special peculiarities of the stock and fuel.

Wet Process.—Here the machinery required is much simpler owing to the soft and fine grained character of the materials.

Marl.	*Clay.*
1. Blunger or wet pan with perforated bottom.	1. Dryer.
2. Tank, kept agitated.	2. Disintegrator.
	3. Bin.

a. Mixer.
b. Tube-mills.
c. Storage and correction tanks.
d. Kilns.
e. Clinker cooler.
f. Kent mill.
g. Wind separator.
h. Griffin mill.

Storing Cement.—The stock house should be large enough to hold at least one month's run of cement. It is preferably built of concrete and divided into a number of bins. By testing the cement in each bin by the usual physical tests, taking care to sample the bin thoroughly, the

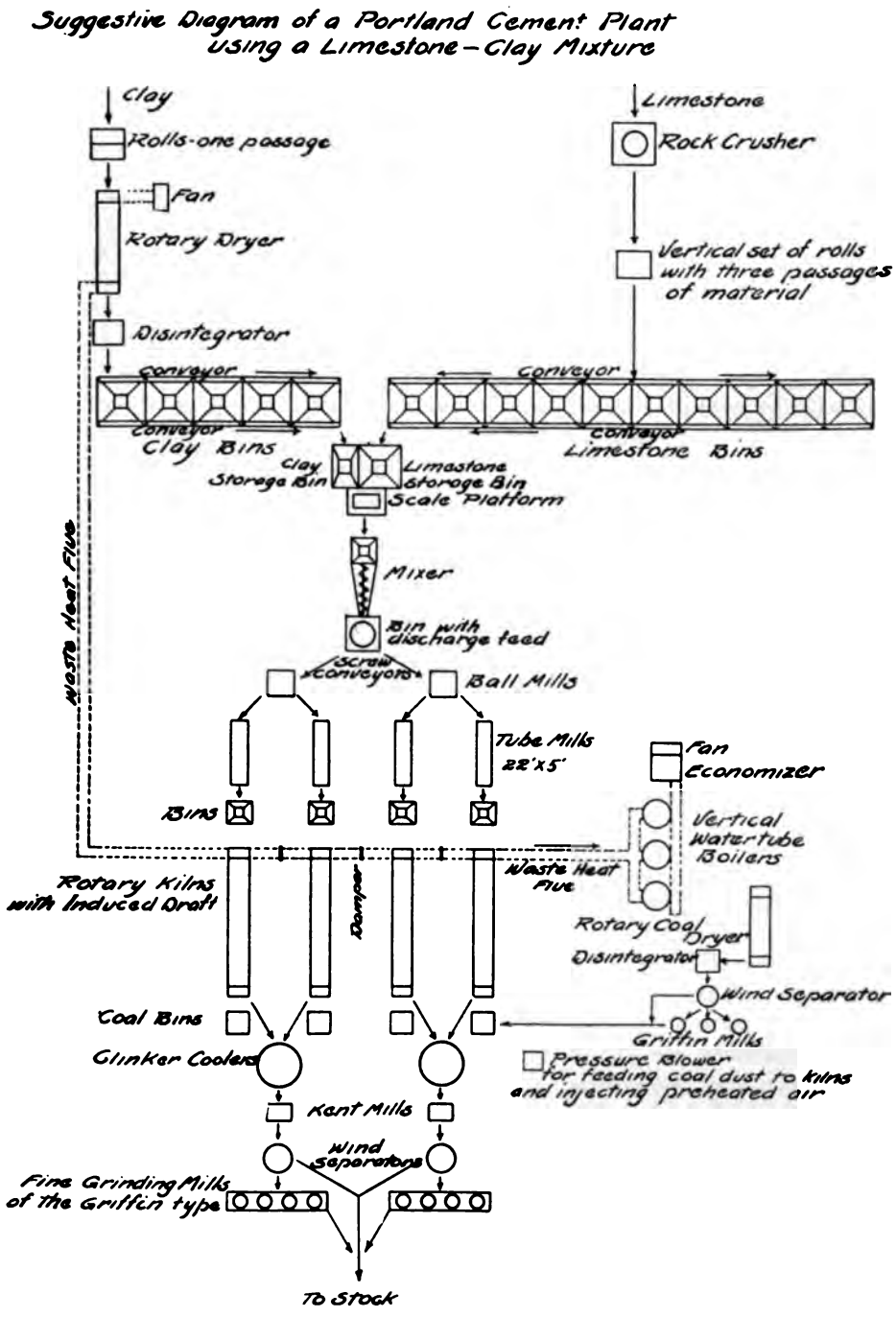

Fig. 60. General ground plan of a Portland cement works, showing sequence of mechanical treatment.

chemist allows the cement in such a bin to be shipped, keeping a record of the tests made. Theoretically, of course, the cement should be kept stored in thin layers to which the air has ready access, but in practice this is difficult to carry out. The bins should have a sloped bottom so that the cement can be discharged by gravity by simply lifting a slide. The packing is usually done at one end of the stock house. In regard to the use of packing machines opinions seem to differ, some advocate them, others think hand packing is just as cheap. Evidently the amount saved, by using machines, if there is any saving, is quite small. Sacks are used mostly at present in place of the barrels which were employed almost exclusively a few years ago.

The net weight of cement in barrels varies somewhat according to whether the cement is packed or is loose. S. E. Thompson found the net weights of cement per barrel to vary from 370.07 to 387.0 pounds. A cubic foot of various Portland cements, packed and loose, was weighed and found to weigh as follows:

	Packed pounds.	Loose pounds.
Giant	113.81	91.38
Alsen	118.45	89.20
Taylors	122.75	94.24
Dyckerhoff	123.16	93.18
Atlas	117.54	100.49
Aalborg	115.71	91.40

The barrels weigh from 21 to 25 pounds. Each barrel is supposed to contain 380 pounds of cement, each sack 95 pounds.

Power Required in Cement Works.—A good basis for estimating the power required is afforded by the figures, already quoted, in part, which represent the power required at the cement works of Wm. Krause and Sons, Martin's Creek, Pa., as determined by actual measurement from the input and output of the electric motors used. The friction load of the plant, main shaft 6 inches in diameter and 240 feet long, is 55 horse-power. Power to drive 4 ball-mills is 155 H. P. or per mill 39 H. P. Five tube-mills use 333 H. P. or 66.6 H. P. per mill.

Each kiln, one revolution per minute, uses 3.7 H. P. A 30 foot belt conveyor for stone, 1.2 H. P.

A stone crusher of a capacity of 25 tons per hour, with its bucket conveyor, 32.6 H. P., maximum load.

Stock house, screw conveyors 450 feet long, 2 barrel conveyors, packers and shafting, 19.5 H. P.

Each figure represents the output of the motor for the purpose designated.

A convenient rule for estimating the power required in cement mills is: One H. P. for each barrel produced per day if marl is used and 1.5 H. P. per barrel per day if rock is worked.

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would have any broad utility, owing to the greatly varying conditions under which different plants must always operate. Neither is it good policy, in the writer's opinion, to publish broadcast ideal figures, which might attract capitalists and lead them to expect extraordinary profits, thus causing overproduction and ruinous competition, such as has been experienced in some cement districts. The profits of the cement business are close and sound management is required. A works not over capitalized and not handicapped by unsuitable conditions, high cost of raw material or of fuel or poor shipping facilities, can expect a fair and constant profit, but soon

Fig. 61. View of the Alma Portland cement plant, at Wellston, Ohio.

it will be a question of the survival of the fittest, just as has been experienced in Germany and other countries. The growth of the American cement industry has been enormous, and in spite of the growing number of uses to which cement is put, the supply will soon be equal to the demand. It is to be hoped that the import of cement to the United States will soon be a thing of the past and that our country will acquire its share of the export trade in our natural markets, South America and the American possessions in the east, as well as in the other markets of the world.

First Cost.—In order to afford some basis of comparison in regard to the first cost of a cement plant the following rough estimates are quoted. Machinery for a two rotary plant, working limestone and clay, about 350 barrels per day of 24 hours.

Number of machines.	H. P.	Approximate Cost of		
		Machinery.	Foundation and Supports.	Erection or Installation.
Raw Material Machinery.				
1 Stone crusher, No. 5	50	$ 1,700	$ 100	$ 50
1 Clay disintegrator	25	750	50	25
2 Driers	20	3,000	600	150
1 Ball mill, 5′ x 10′	50	2,800	125	75
1 Tube mill, 5′ x 22′	50	2,700	125	100
	205	$10,950	$1,000	$ 400
Calcining Machinery.				
2 Rotary kilns, 6′ x 60′	15	6,200	400	300
Bricks for lining and setting kilns	....	800	.....	250
1 hot clinker elevator	5	400	40	50
1 Clinker cooler	5	1,300	75	50
	25	$ 8,700	$ 515	$ 650
Clinker Grinding Machinery.				
1 Ball mill, 5′ x 10′	50	2,800	125	75
1 Tube mill, 5′ x 22′	60	2,700	125	100
	110	$ 5,500	$ 250	$ 175
Elevating and Conveying Machinery.				
3 Elevators (iron casings)	15	1,200	75	150
Conveyors, approximately	25	500	50	75
	40	$1,700	$ 125	$ 225
Summary.				
Raw material machinery	205	10,950	1,000	400
Calcining machinery	25	8,700	515	650
Clinker grinding machinery	110	5,500	250	175
Elevating machinery	40	1,700	125	225
	380	$26,850	$1,890	$1,550

It is generally estimated that a seven rotary kiln plant with a capacity of 1,200 barrels per day, working limestone and clay, can be put up for $300,000.

In regard to the cost of producing cement a number of estimates have been published, several of which are given for what they are worth, but the writer declines to express any opinion of them. They should be accepted with caution, as they all tend to underestimate the actual cost.

Estimate No. 1, Limestone and Clay.

Limestone crushed	per barrel	$0.05
Clay	per barrel	.02
Labor	per barrel	0.15
Fuel	per barrel	0.20
Supplies and repairs	per barrel	0.12
Cost per barrel, not including office and selling expenses		$0.54

Estimate No. 2, Cement Rock and Limestone.

Maximum capacity 2,000 bbls. per day, average capacity 1,200 to 1,300 bbls.

Help needed:

Crushing and drying	for each shift,	2 men
Raw and clinker grinding	for each shift,	6 men
Coal grinding	for each shift,	3 men
Rotary kilns	for each shift,	6 men
Power house	for each shift,	5 men
Unloading coal, stone, etc		12 men
Machine shop, electricians, smiths, and bricklayer		12 men

For laboratory and office expenses 2 cents per barrel is reckoned.

The coal for firing the kiln is 13.35 cents per barrel, for the boilers and dryers 10.9 cents per barrel.

The total cost per barrel would now be distributed as follows:

Labor:		
Quarry	$0.050	
Crushing and drying	0.005	
Grinding	0.015	
Burning	0.015	
Power generation	0.011	
Coal grinding	0.010	
Yard work	0.015	
Machine shop	0.0225	
Miscellaneous	0.0025	$0.15
Raw Materials:		
Coal	0.2250	
Gypsum	0.0125	0.245
Accessory Expenses:		
Repairs	0.04	
Oil	0.02	
Miscellaneous	0.03	0.09
Packing and loading	0.04	
Works management	0.02	0.06
Interest on investment ($700,000)	0.07	
Sinking fund and deterioration	0.10	
Management and selling expenses	0.065	0.235
Total		$0.7775

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In volume VIII, Michigan Geological Survey, the following figures are given regarding the cost of making cement in a marl and clay installation, by the wet process: the burning is estimated at 17.2 cents per barrel, the clinker grinding at 8.8 cents, the power at 9.3 cents and the packing at 2.55 cents per barrel. The average cost of making cement in Michigan is estimated at 68 cents per barrel.

OHIO PORTLAND CEMENT PLANTS.

The writer has visited all the cement plants of Ohio with one exception and was received with courtesy and consideration in every plant visited. The pioneer plant of the State is that of the Sandusky Portland Cement Co., at Bay Bridge. Permission to visit this plant was refused, hence no description can be given of its equipment or arrangement.

The largest cement works of the State, the Castalia Portland Cement Co., is located at Castalia, 6 miles south of Sandusky, in Erie county. The raw materials are a very pure travertine, and a soft clay. The travertine is the only deposit of the sort worked in the United States. The wet process is used, the materials being run through a wet plan and tube mills. After being ground the slurry is pumped into large tanks by means of compressed air and the composition corrected by the addition of high lime or high clay correction slurry. The burning is done in 13 rotary kilns. The clinker is ground in ball and tube-mills, and two Griffin mills are also installed. The coal is ground in Griffin mills. The power available is 1,700 horsepower. The average capacity is 1,500 to 1,600 barrels of high grade cement. A view of this plant will be found on page 332, for which the writer is indebted to the company. The offices of the company are at Pittsburg, Pa.

In Stark county, at Middle Branch, we find the Diamond Portland Cement Co. using the Putnam Hill limestone and the shale associated with it, of which, however, part is rejected and dumped. This mill has a capacity of about 600 barrels per day, using 8 to 10 feet of the shale and 6 to 7 feet of the limestone. The limestone is crushed by Aultman rock crushers and then passes through a rotary dryer, roller crushers, and is ground fine by Emery mills. It is then stored in large tanks, 28 feet by 10 feet, being thoroughly sampled in these and analyzed.

The shale is put through a dry pan, a rotary dryer, and is ground fine like the limestone and is also stored in large tanks where its average composition is determined. The limestone and shale are then weighed out by means of a bucket and crane and ground together in large ball-mill mixers. The mixture is hence positive and is bound to be correct. The mixed constituents are then conveyed to a large storage tank, which feeds a pug-mill and auger brick machine where stiff mud bricks are made and stacked on iron cars. These are run on tracks into a steam tunnel dryer and dried thoroughly. The dried bricks are

Fig. 62. View of the Castalia Portland cement plant, at Castalia, Ohio.

hoisted and dumped into three large, double Dietzsch shaft kilns, where they are burnt to vitrification. The clinker is crushed in an Aultman reducer and ground in ball and tube mills. Packing machines are used. The chemical and physical laboratories are exceedingly fine and well equipped.

Extensive changes have recently been made in the plant, bringing in the most modern features.

In Logan county there are two plants, one the old established works of the Buckeye Portland Cement Co. at Harper, the other a newer concern, the Alta Portland Cement Co., at Rushsylvania. The Buckeye works represent a gradual growth from the German type of plant to the new American method. First, a double Dietzsch kiln was used, to which later were added four continuous shaft kilns patterned after the kiln designed by Candlot, France, and still later rotary kilns were installed. The raw materials are a fine grained marl and very fine glacial clay. Two methods were employed when the writer visited the plant, one supplying bricks to the shaft kilns by blending the clay and marl in a wet pan and making the bricks on an auger machine, which are then dried and taken to the kiln, and the other producing slurry for the rotaries by grinding in a wet grinder. The slurry is pumped into storage tanks, kept agitated, and from these to the rotaries. The clinker is crushed by roller crackers and finished in part by mill stones and partly by tube mills. At one time producer gas was used for burning one rotary kiln, which was a success, but not as economical as coal dust firing. This plant recently has undergone further changes and has received many new features. The marl is dredged and hauled to the factory in tram cars.

The works of the Alta Portland Cement Co. are but two miles distant from the Buckeye plant and practically the same raw materials are worked, which are hauled by a steam locomotive in iron dump cars. The slurry process is used, the grinding being done in two tube mills which feed two rotary kilns. Storage tanks provide for a good reserve stock of ground raw material. The clinker is ground in ball and tube mills and the coal by an æro pulverizer. The cement stock house consists of three stories, the cement gradually falling from one story to the other, thus giving it a better chance to cure. At this plant the raw materials are dug by hand. The capacity is about 300 barrels per day, the available power being 300 horsepower.

At Wellston there are also two plants, the Alma Cement Co. and the Lehigh Portland Cement Co., formerly the Wellston Portland Cement Co. The first, destroyed by fire several years ago, has been rebuilt with the most modern improvements. The accompanying plan of this mill shows the arrangement of the machinery and kilns and hence needs no description. The dry process is used; the raw materials are limestone,

shipped several miles from Cornelia furnace, and a clay obtained near the plant. This company also owns its own coal lands; hence the fuel question is not a troublesome one. The laboratory facilities are generously provided for. As to shipping facilities, they could not be improved upon, and there are probably few cement works who can boast of as many connections with different railroads. This shows the wisdom of building the plant at this place instead of erecting it at the limestone quarry. The mill has 8 rotaries and an approximate capacity of 1,400 barrels. For the plan of the works the writer is indebted to the Henry S. Spackman Engineering Co., Philadelphia, who constructed the plant.

Fig. 63. View of the Lehigh Portland cement plant, at Wellston, Ohio, when first constructed.

The Lehigh Portland Cement Co. works practically the same raw materials. The stone and clay pass through a Gates crusher together and then through a rotary dryer; from here the mixture passes through a Williams pulverizer into tube mills driven direct by electric motors. The rotary kilns are 60 by 6 feet. The clinker is ground, or was at the time of the visit, by a Williams mill and tube mills. Electrical transmission is used throughout and hence no belts are seen except in engine house. The available power is 700 horsepower.

At Ironton a new plant has been erected, that of the Ironton Portland Cement Co., using the limestone found at this place, and clay. The materials are ground in a Gates crusher, a Williams mill and tube mills, and the clinker passes through a Kent mill, replacing ball-mills, and finally through tube mills.

Electric transmission is used satisfactorily and flexible connecting shafts have proven very successful. The raw materials are dried in a rotary dryer. The capacity of the plant is about 500 barrels per day.

The southeastern part of Ohio offers a good field for the establishment of cement plants, owing to the cheap raw materials and especially cheap coal, together with good shipping facilities. It is a field which is bound to be more and more developed as the confidence in the cheapness of the dry process increases, and it is more fully realized that dry grinding produces a cement equally as good as the marl cements made by the slurry process.

CHAPTER IX.

THE PROPERTIES OF PORTLAND CEMENT AND THE TESTING OF CEMENT.

The subject will be considered under the following headings:

1. Hydration and heat of hydration.
2. Setting and hardening.
3. Tensile and crushing strengths.
4. Constancy in volume.
5. Specific gravity.
6. Fineness of grain.
7. Some physical and chemical constants.
8. The effect of various reagents on the properties of Portland cement.
9. The enduring qualities of Portland cement with special reference to the action of sea water.
10. American standard specifications.

HYDRATION.

1. On adding water in proper quantity to Portland cement it is found to stiffen gradually until it becomes so hard that the mass cannot be penetrated by a rod. Under the microscope white, needle-like crystals of calcium hydrate are seen to grow rapidly, and the grains of cement appear to swell, forming a mass of colloid particles. The phenomenon of hardening must, in the nature of the case, be strongly analogous to the crystallization of supersaturated solutions.* The more the crystal surfaces in contact are developed, the greater the total adherence and the strength of the mass. Crystals in long plates or in interlocked fibers should give greater strength than blunt and heavy crystals. But the result of this crystallization depends on many factors, the degree of supersaturation, i. e., the amount of water present, the fineness of the salt and many other conditions. At the same time the production of the colloid particles, distinct from the crystals of lime hydrate, raises the question whether the hardening due to hydration might not be due to the drying of the greater mass of colloid material. This question has not as yet

*Chatelier, *Engineering Congress*, Chicago, 1893.
Trans. Am. Inst. Min. Eng., 1893.

been answered and we do not know whether the resulting hardness is due to the sum of the effects of the crystallization and the colloid hardening or of one of the two, just as we are in ignorance as to the cause of the plasticity of clay, in regard to which, however, the colloid theory is offering the most powerful evidence.

On the other hand it has been shown that when cement is made up with water, its electrical conductivity is much greater if a current is conducted through it than if the latter were simply passed through the solution which was in contact with the cement, and in which the latter had been thoroughly shaken. At the moment of hardening the electric resistance increases enormously. This thus offers some additional evidence in favor of the supersaturation theory. Whatever the results of the hydration may be, we know that the crystalline mass of the hydrolite breaks down by hydration to simpler compounds and calcium hydrate. We have hence a certain amount of water of hydration. At the same time a slight increase in temperatures is observed; that is, some heat of hydration is evolved. The amount of water of hydration found in Portland cement varies greatly and depends on the conditions of fineness, the amount of water added, etc. The writer, by heating hardened cement pats in a hard glass tube in an atmosphere of air freed from carbon dioxide and water, up to red heat, was unable to obtain consistent results. On using a little more or less water, making a larger or smaller pat, different amounts of water of hydration were found. Zulkowski takes 14.67 per cent. of water to be theoretically correct for ideal Portland cement. S. B. Newberry found from 10 to 27 per cent. of water, Feichtinger 11.56 per cent. Probably Zulkowski is nearest to the truth, especially since one of his assistants actually found in a Portland cement 14.44 per cent. of water of hydration.

In regard to the heat of hydration a number of commercial American Portland cements were taken and tested in the calorimeter already described, using from 5 to 10 grams in 100 cc. of distilled water. The results obtained were as follows:

Number.	Calories per gram.	Number.	Calories per gram.
1	1.79	8	5.56
2	1.19	9	3.43
3	0.47	10	6.41
4	2.00	11	1.35
5	0.50	12	3.98
6	2.10	13	1.04
7	2.20	14	1.19

No attempt was made to take into account the heats of the solution.

We note here values running as high as 6.41 and as low as 0.47 per cent., but considering the many possible factors entering into the reaction it is a significant fact that the thermal values are quite low, not exceeding 10 calories. Now we might be led to the general conclusion that the higher calorific values are simply due to the hydration of the excessive amount of calcium oxide present. But we have no right to make such an assertion, and, furthermore, experiments quoted elsewhere have shown that the amount of lime contained in a cement stands in no direct relation to the heat evolved. Certain factors like the amount of silica present have a great influence on the heat of hydration. But taking the same cement, with the same clay base, the case is different. Here we may be able to detect any uncombined lime due to insufficient curing or underburning, and, hence, for a given cement we can establish a certain thermal limit and the calorimeter becomes a valuable aid. The significant fact is also to be noted here that aluminous cements show high heats of hydration which drop at once as soon as the clay base is enriched in silica. It cannot be denied that in doubtful cases where the boiling test is questioned the calorimeter is able to give important contributory evidence. The calorimeter or an equivalent instrument should therefore form a valuable adjunct of every cement laboratory. Tetmayer has designed an instrument which is to be used in conjunction with the Vicat needle, which consists of a hard rubber casing and rubber cover through which the thermometer is inserted and its readings noted, while in the meantime the time of setting is observed by means of the needle. This test is employed by a good many cement manufacturers, and the writer was told by several superintendents that they never allow cement to leave the stock house unless its rise in temperature on setting falls below a given limit. It is a curious fact that a second rise in temperature takes place with some cements, which often is quite considerable, up to 7 or 8 degrees Centigrade. Just in how far this is related to the setting has not yet been determined. The curves of figure 64 show the temperature changes observed in four American cements.

SETTING AND HARDENING.

These two stages must be clearly distinguished. The first represents but a short period, from 15 minutes to 12 hours, while the second may extend for a period of years. If cement is made up with from 25 to 34 per cent. of water, mixed thoroughly for about three minutes and made up into a pat, it will be found that after some time it begins to stiffen so that it becomes more and more difficult for a needle to penetrate into the mass. This first period of the hardening we call setting and its beginning is determined by the point at which a wire, 1-12 of an inch in diameter, loaded with ¼ pound, is supported by the cement without in-

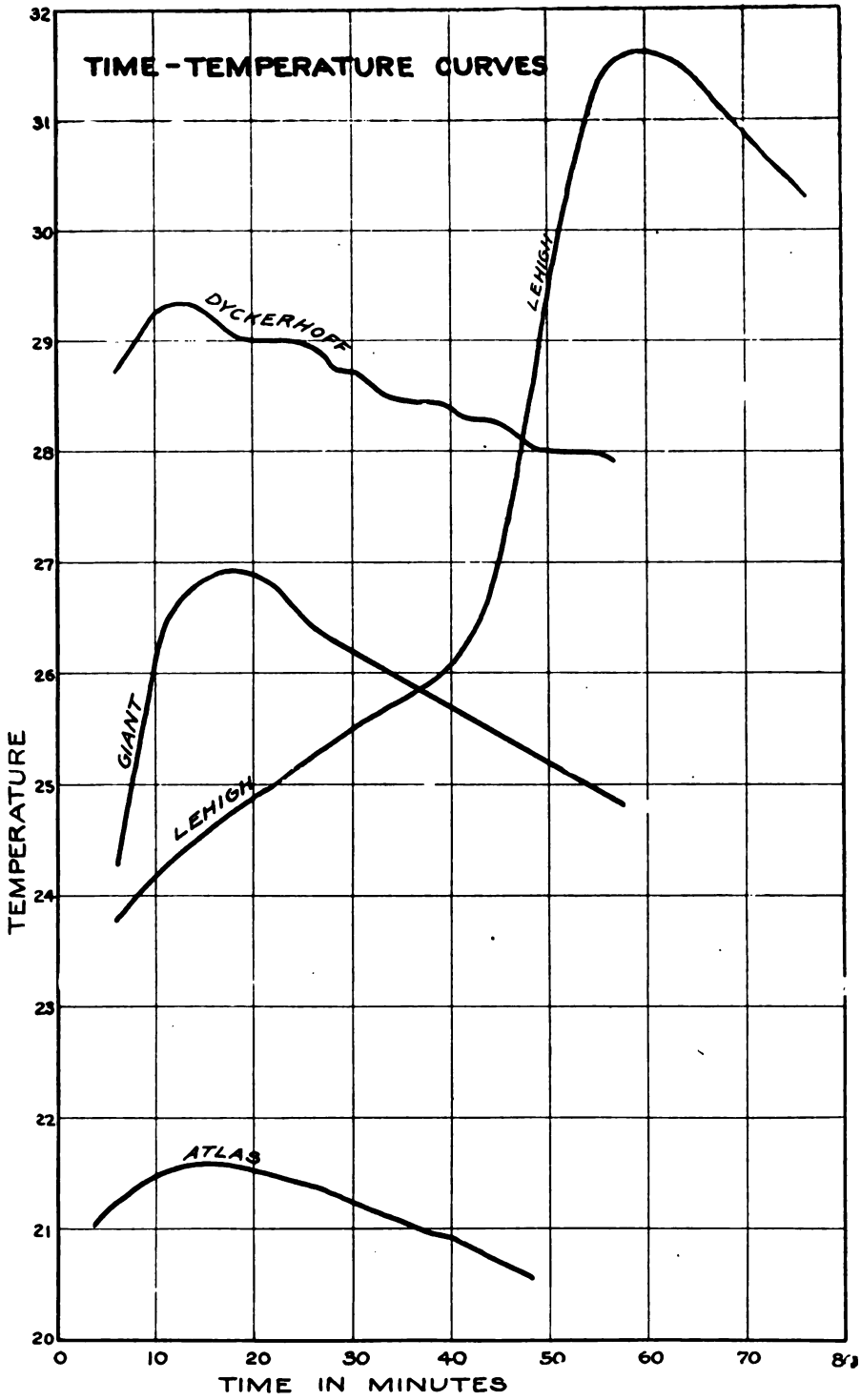

Fig. 64. Curves showing heat evolved in setting, as observed in four typical American plants.

denting the surface, while the close of the setting is fixed by the point at which a wire 1-24 of an inch in diameter no longer indents the cement. Starting from this condition the cement gains in hardening for one or more years. In European practice the Vicat needle is employed exclusively for the determination of the time of setting. This instrument consists of a weighted cylindrical rod which slides up or down in guides and is provided with an indicator and set screw. (See Fig. 79, p. 372). The cross section is 1 sq. cm. and the weight of the rod is 300 grams. The cement is molded in a conical receptacle, 65 mm. in diameter on top and 75 mm. at the bottom and 40 mm. high. If the rod penetrates 5 to 7 mm. the cement is said to have standard consistency. The lower part of the rod is now replaced by a needle 1 sq. mm. in cross section and enough weight is added to keep the total weight equal to 300 grams. As soon as the needle cannot penetrate the cement complete setting is said to begin, and when it cannot penetrate the mass at all the final setting is considered finished. Some advocate the use of thermometric measurements in place of the needle tests, considering the setting finished when the temperature of the cement begins to fall. This, however, is quite liable to be erroneous and deceiving.

The rapidity of the setting of cement is influenced by a number of factors, which are as follows:

1. Amount of water used.
2. Temperature of water and air.
3. Fineness of the cement.
4. Composition of the cement.
5. Time and manner of curing cement.
6. Catalytic agents added to the cement.
7. Composition of the water.

In brief, the more water is added above the amount required, the slower will be the setting.

Warm water invariably hastens the setting and it has been found by Erdmenger that lukewarm water also increases the ultimate strength of the cement. Boiling water, on the other hand, decreases the strength of the cement, owing to increased porosity. Cold water causes the setting to take place more slowly, as we find it to be true in most of the chemical reactions.

Fine cement invariably sets faster than coarse cement.

As we have seen already, aluminous cements set very quickly, as well as cements high in lime, while, on the other hand, silicious cements tend to set slowly.

Cement fresh from the kiln is much more rapid than cement which has been cured. This is due to the slaking of any uncombined lime as well as to the absorption of carbon dioxide. Cured cement when heated strongly resumes its initial rapidity of setting. Slow setting cement

exposed to the sun frequently becomes quicker in its action. This is due to the breaking down of the coarser particles to dust, a tendency shown by practically all cements, for even coarse clinker will in time break down to a powder.

It has been known for a long time that small amounts of certain salts added to Portland cement affect the time of setting in a most decided manner. Thus the effect of different chlorides added to a Portland cement, whose setting time was 12 minutes, was as follows:

Name of Substance.	1 per cent.	2 per cent.	3 per cent.	4 per cent.	5 per cent.	6 per cent.
	Minutes	Minutes	Minutes	Minutes	Minutes	Minutes
Magnesium Chloride.....	29	35	55	75	120	260
Barium Chloride.....	45	125	200	340	465	580
Sodium Chloride.....	32	65	100	150	270	330
Ammonium Chloride.....	31	45	85	100	200	270

Some contradictory facts are, however, noticed in this connection, Thus a dilute solution of calcium chloride retards the setting, a concentrated solution accelerates it. Soda and potash solutions accelerate the setting.

The best work on this subject has been probably done by Dr. Rohland, who ascribes the action of various small amounts of salts to catalysis and gives expression to the following statement:

Where the velocity of reaction setting is very slow the catalytic agent produces a greater effect than when the velocity is greater. Positive (accelerating) and negative (retarding) reagents may neutralize each other. The quantities may be very small; 1 per cent and less is often sufficient to produce great changes. He makes a list of catalytic agents including:

Calcium sulphate,	—
Aluminum chloride,	+
Sodium carbonate	+
Calcium chloride	+
Barium chloride	+
Potassium bichromate	—
Sodium chloride	o

He also brings out the fact that aluminates in cement may decompose on storing and thus bring about changes in the rate of setting, so that sometimes in spite of curing the cement becomes quicker setting. The

best example of catalytic action we have in the addition of gypsum to the ground clinker.

It has been found by experience that hard water tends to retard the setting, which also applies to sea water.

In general it may be said that slow setting cements result as a rule in stronger and more consistent cements than quick setting cements. The same statement also applies to the hardening. Cements which assume their maximum hardness in a short time are liable to go back in their strength, as has been shown by many tensile and crushing tests.

TENSILE AND CRUSHING STRENGTH.

In use, cement is largely subjected to crushing strains, and hence crushing tests would seem the legitimate mode of testing cement, but owing to the expensive apparatus required in making these tests, the tensile strength of a cement is normally taken as the criterion of its strength. Roughly speaking, the crushing strength is from 10 to 12 times the value of the tensile strength.

The tensile strength test is carried out by filling brass molds of the well-known figure 8 shape with a paste consisting of the cement to be tested, either mixed with sand of certain definite quality. The molds are filled either by hand or by means of a machine. The briquettes thus made are kept in moist air for 12 to 24 hours, when they are immersed in water, in which they are kept till it is desired to test them, usually from 7 to 28 days. New cements in regard to which but little is known are tested frequently for longer periods—a year or more.

Testing Machine.—The briquette, whose area at the narrowest point is one square inch, after hardening, is put into the tensile strength testing machine and broken at the weakest point. In American practice the type of machine, like the Fairbanks, Fig 65, in which shot is allowed to flow into a balanced bucket until the pressure, multiplied by levers, is sufficient to break the test piece commonly employed. The flow of shot is stopped automatically on the breaking of the briquette, and by weighing the charge of shot run in the pressure on the briquette may be read off. Other machines like the Riehle depend on the gradual movement of a weight towards the end of a lever till the briquette is broken when the weight has arrived at a certain point. Again other machines employ hydraulic pressure, but the one most commonly employed is the Fairbanks type.

In reporting results of tensile strength tests all values of poorly fractured briquettes should be rejected. In practice the tensile strength results vary as much as 18 to 20 per cent above or below the average and are much less consistent than the crushing strength tests. The effect of the kind of sand upon the tensile strength is exceedingly marked, and variations in the results are greater than in the crushing tests, though, of

course, the general laws governing the sizing of the sand and the porosity with reference to the ultimate strength hold good for both kinds of tests. But, to illustrate, when clay is added to a sand used in making tensile tests the strength apparently is raised considerably, while with the same sand mixture the crushing strength, if it rises at all, shows but a small increase.

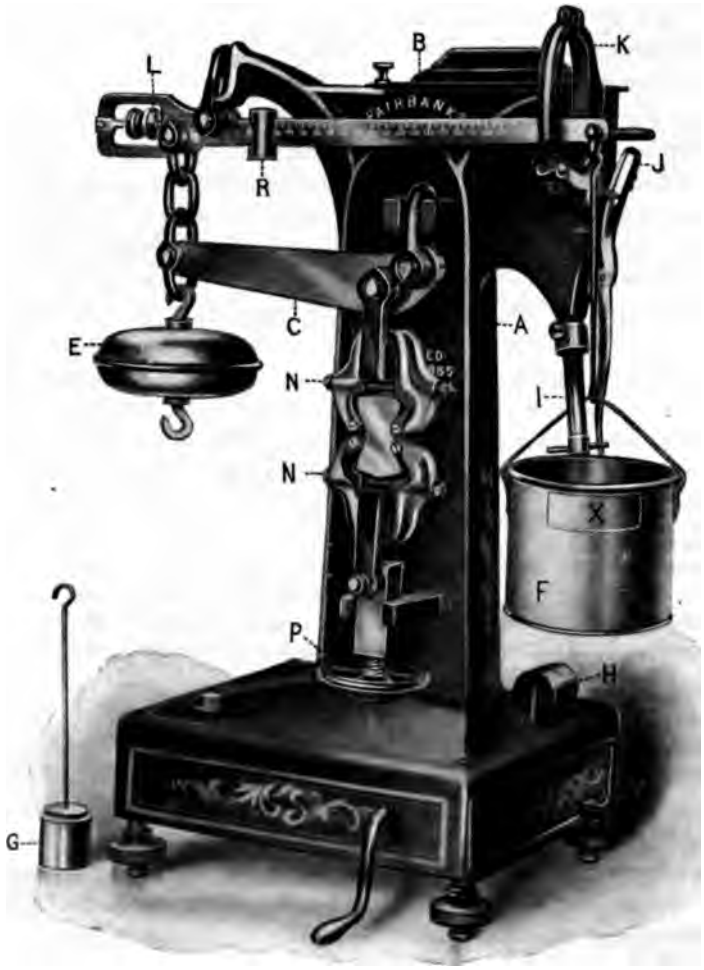

Fig. 66. Amsler-Laffon machine for crushing test.

The tensile strength of neat cement increases up to about one year, but it reaches its ultimate strength quite closely in three months. The tensile strength of the neat cement may vary from 600 to 1,100 pounds after three months in water. The crushing strength of neat cement may vary from 7,500 to 14,500 pounds per square inch after three months. Any decrease in the tensile strength of cement shows the presence of mechanical strains in the test pieces or chemical changes, and such

cements are open to suspicion. Indirectly the tensile strength is a test for fineness of grinding, for, given a certain cement, it will show a greater tensile strength the finer it is ground. Silicious cements are occasionally looked upon with distrust owing to their comparatively low tensile strength in the short time tests. This, however, is due to the slower hardening of these cements and not to any inherent weakness, for they show an exceedingly high tensile strength after three months, the writer recollecting several instances in which silicious cements pulled considerably higher than 1,000 pounds, neat.

On the other hand, aluminous cements show a very high initial tensile strength, but after some time a significant decrease in strength is observed, which not uncommonly results in the destruction of the cement structure. It is, hence, always preferable to use a cement showing a steady increase in strength, though the initial strength may not be high. Very high initial tensile strengths are to be regarded with suspicion and will be found to be indicative of weakness rather than strength. In American practice crushed quartz not coarser than 20 mesh and not finer than 30 mesh is used as the standard sand and though, owing to the large proportion of voids, it does not produce the densest and hence strongest mixture, it affords a uniform standard of comparison. The following table indicates the required tensile strengths in American practice:

A.—Neat cement.
1 hour in air, 23 hours in water, 100–140 pounds per square inch.
1 day in air, 6 days in water, 250–550 pounds per square inch.
1 day in air, 27 days in water, 350–700 pounds per square inch.
1 day in air, 364 days in water, 450–800 pounds per square inch.

B.—One part of cement (by wt.) to three parts standard sand.
1 day in air, 6 days in water, 80–125 pounds per square inch.
1 day in air, 27 days in water, 100–200 pounds per square inch.
1 day in air, 364 days in water, 200–350 pound per square inch.

To indicate how American cements run, the breaking figures of a well-known cement might be quoted,* which are interesting, since they represent the averages, of many tests. The briquettes were made of Giant cement, with standard sand in the proportion of 1 cement: 2 sand.

Time.	28 days.	3 mos.	6 mos.	9 mos.	12 mos.
Number of breakings	690	215	185	155	165
Aver. break. weight, pounds per sq. inch.	441	563	657	671	663

*C. S. Gowen, *Proceedings, Amer. Society for Testing Materials* July, 1903.

Amount of Water.—The amount of water used in making the mortar has considerable influence on the resulting strength, as is indicated by the following series of tests made by E. S. Larned:*

Portland Cement Brand.	Per cent. of water used.	Initial set. Minutes.	Final set. Minutes.	Tensile strength neat cement. Pounds per square inch.					
				24 hours.	7 days.	28 days.	3 months.	6 months.	12 months.
Giant ...	15	12	207	371	655	875	941	720	787
" ...	16	29	297	303	750	973	1008	735	816
" ...	18	80	355	260	649	773	831	645	748
" ...	20	142	402	233	500	693	716	621	676
" ...	22	268	473	184	546	635	658	601	589
" ...	24	327	912	167	539	649	644	629	755
Atlas	13	13	270	366	775	859	1067	892	832
" ...	14	18	303	404	780	891	972	852	781
" ...	16	22	327	363	602	725	844	806	723
" ...	18	15	383	308	570	723	785	728	724
" ...	20	56	703	225	590	718	760	674	636
...	22	52	833	166	554	649	731	643	604
" ...	24	188	918	42	510	691	695	632	574

The proper amount of water to be used with each cement must be determined by experience.

Crushing Machines.—The crushing test is ordinarily performed on a very elaborate and expensive machine which can be employed only in large laboratories and testing stations.

However, there are certain machines on the market that permit of carrying out crushing tests, such as the Amsler-Laffon, which are not too expensive and still give good results. The machine mentioned is hydraulic in principle and uses as liquid heavy glycerine which does not leak between the piston and the cylinders. Pressure is applied by moving the piston by means of a geared crank and compressing the liquid. The pressure is indicated by a mercury manometer. In principle as well as in design this machine is a most excellent apparatus, eliminating the usual errors of hydraulic machines of this kind most completely. It de-

*American Society for Testing Material, July, 1903.

serves much more extended use than it has been receiving so far in American practice.

Crushing tests are superior to tensile strength tests in more than one respect. They not only indicate the true strength of the cement, but also are not so liable to experimental errors.

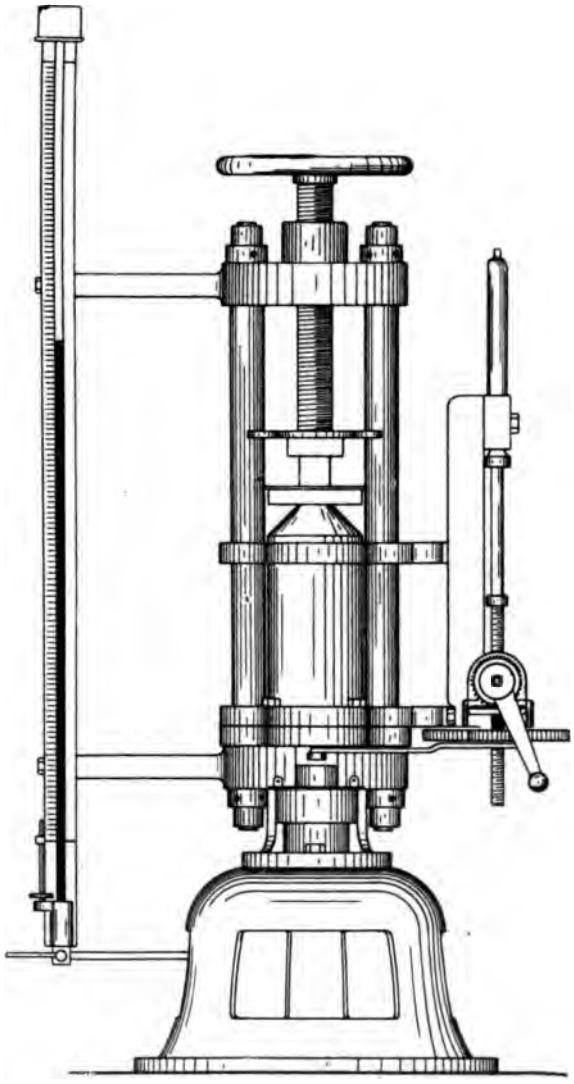

Fig. 66. Amsler-Laffon machine for crushing test.

Larger hydraulic machines for testing concrete cubes are now also on the market at prices within the reach of many testing laboratories. Testing machines depending on screw pressures and spring manometers are as a rule less reliable than the hydraulic machines.

Both the tensile and crushing strengths vary with the same cement, due to the influence of several important factors, which are:

1. Amount of water used.
2. Kind of sand employed.
3. Mode of preparing the test piece.

Amount of Water.—In German practice the proper proportion of water for a given 1:3 mixture is determined by mixing the sand and cement, dry, in a standard mixer, adding water, mixing wet for ½ minute,

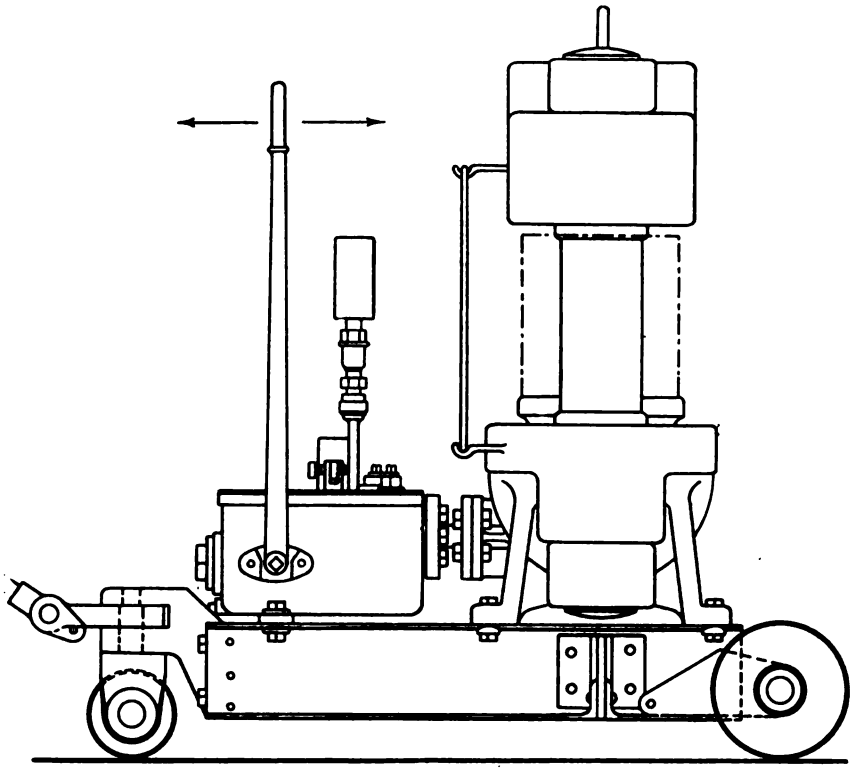

Fig. 67. Portable machine for crushing large concrete cubes.

and transferring to a cubical mold provided with a top plate. This plate is now subjected to a number of blows from a standard hammer and if between the 90th and 110th blow cement paste begins to leak out of the mold box the amount of water is considered sufficient. If not, another batch of cement is made up with more water. By experience, however, it becomes possible to tell without any elaborate apparatus just when the proper amount of water has been added. If an insufficient amount of water is used, hydration will not take place to its full extent and hence the cement will be weaker than its normal strength. If too much water is used the resulting porosity will be too great and hence the strength is again decreased.

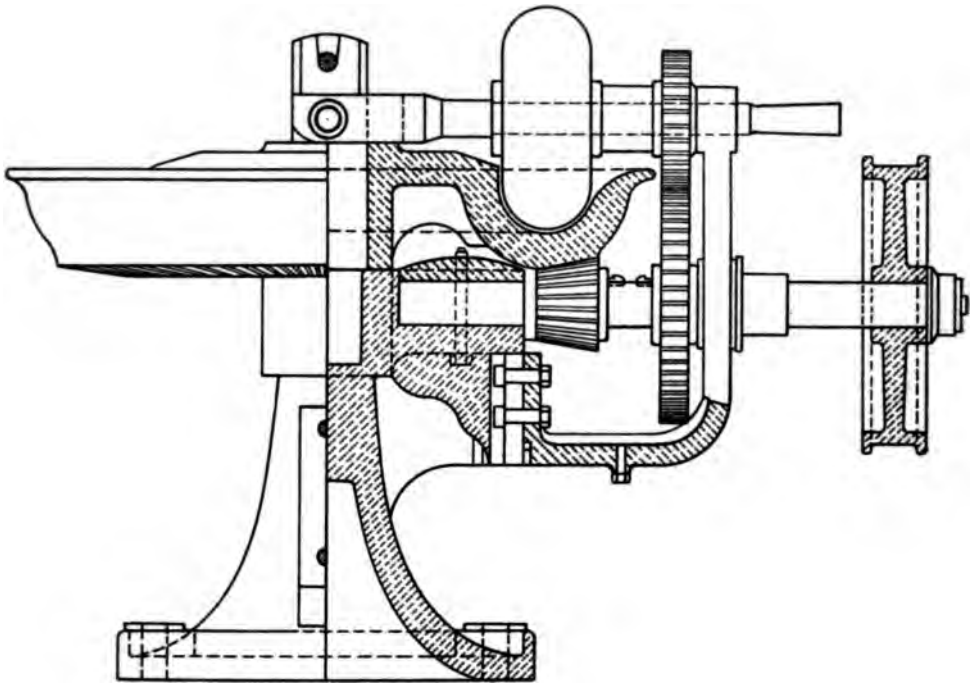

Fig. 69. Steinbrueck mixer for preparing cement mixtures for test.

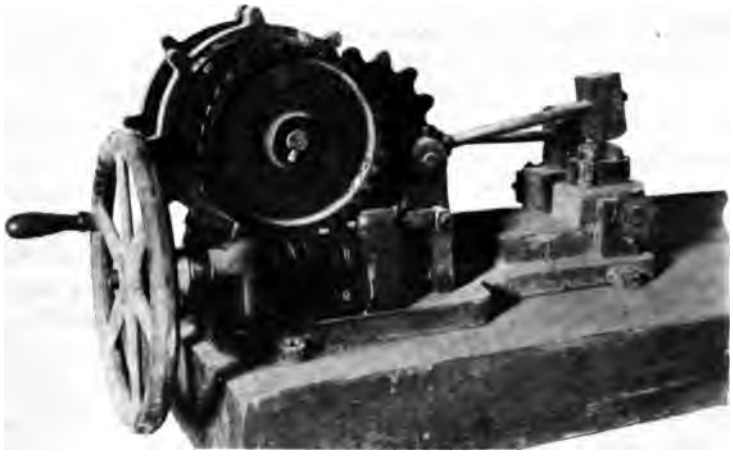

Fig. 70. Boehme hammer, for compacting cement in molds with uniform density.

In order to illustrate, first, the relation between tensile and crushing strength, second, the strength of neat and sand mortar, and, third, the relation between water and air hardening, the following results obtained by Tetmayer are given, representing the average strengths of 16 Swiss Portland cements:

Time of hardening.	Kind of mortar.	Condition of hardening.	Tensile strength lbs. per sq. in.	Crushing strength lbs. per sq. in.	Ratio of crushing strength to tensile strength.
7 days	neat cement	in water	479	5,754	12.01
28 days	do	do	552	8,108	14.69
84 days	do	do	593	9,699	16.36
210 days	do	do	589	12,547	21.31
365 days	do	do	633	14,346	22.67
7 days	1 cement : 3 sand	in water	293	3,033	10.35
28 days	do	do	372	4,014	10.79
84 days	do	do	462	4,970	10.75
210 days	do	do	520	5,859	11.27
365 days	do	do	604	6,319	10.46
7 days	1 cement : 3 sand	in air	314	2,979	9.49
28 days	do	do	418	3,935	9.41
84 days	do	do	452	4,450	9.85
210 days	do	do	508	4,605	9.06
365 days	do	do	621	5,143	8.28

CONSTANCY OF VOLUME.

Portland cements are liable to the following changes in volume:

1. Increase in volume when hardening in water.
2. Decrease in volume when hardening in air.
3. Change in volume due to changes in temperature.
4. Decided and irregular increase in volume due to abnormal conditions.

1. It has been found in extensive tests made by Dr. Schumann that of eight cement mortars, 1:3, hardening in water, all showed an increase in volume. Expressed in terms of the linear expansion for a test piece 10 cm. long, the average increase in length was, after 7 days, 0.0123 per cent., after 4 weeks 0.0051 per cent., after 13 weeks 0.0025 per cent., after 26 weeks 0.0029, after 52 weeks 0.0052, after 2 years 0.0016 per cent.

2. When hardening in air the average linear shrinkage of four Portland cement mortars after three weeks was 0.0417 per cent. on a prism of 10 cm. length. This change of volume is, of course, normal and due to the peculiar colloidal properties of cement.

3. The change in volume due to change in temperature cement has in common with all other bodies. The coefficient of expansion of Portland cement concrete is from 0.0000137 to 0.0000148.

4. The irregular increase in volume due to abnormal conditions in the Portland cement is a great source of danger in using cement and may be due to either of the following causes:

1. Excess of lime present.
2. Large amount of alumina present.
3. Coarse raw grinding.
4. Coarse clinker grinding.
5. Presence of excessive amounts of sulphates or magnesia.
6. Underburning.
7. Insufficient storing.

Such a cement is said to be inconstant in volume, and for the detection of such materials many tests have been proposed and a great deal of literature exists on this point. The matter of testing cements quickly in this respect is far from being settled. The most accurate methods of determining undue increase in volume in hardening are based on direct measurements of the expansion and the best known instruments for this purpose are the Bauschinger and the Martens apparatus.

The first is simply a micrometer which measures the length of a bar of cement mortar about 10 cm. long, exact to 1-200 mm. The second instrument measures the length of a bar either in air or water by means of a steel point which touches the specimen on the one hand and is connected with a rhombic piece of steel on the other. An increase in length will move the rhombic tongue, and with it a long pointer. The instrument virtually compares the changes in length of the test piece with those of the steel part, and since the two coefficients are practically alike fluctuations in temperature have but little influence on the exactness of the readings.

Accelerated Tests.—But the use of these instruments requires a long time, and for practical purposes where results must be had quickly and without the use of delicate apparatus they are not very suitable, especially in the hands of the untrained manipulator. For this purpose, hence, other tests have been employed, and of these the following are the most important:

1. Boiling test, 3 to 6 hours.
2. Steam test, 3 to 6 hours.
3. Warm water test, 24 hours.
4. Normal water test, 28 days.

It is the object of these tests to accelerate the slaking of the quicklime, if any be present in the cement, or the breaking down of the aluminates or imperfect hydraulic silicates, and thus bring about the destruction of the cement or produce evidence of disintegration. They are carried

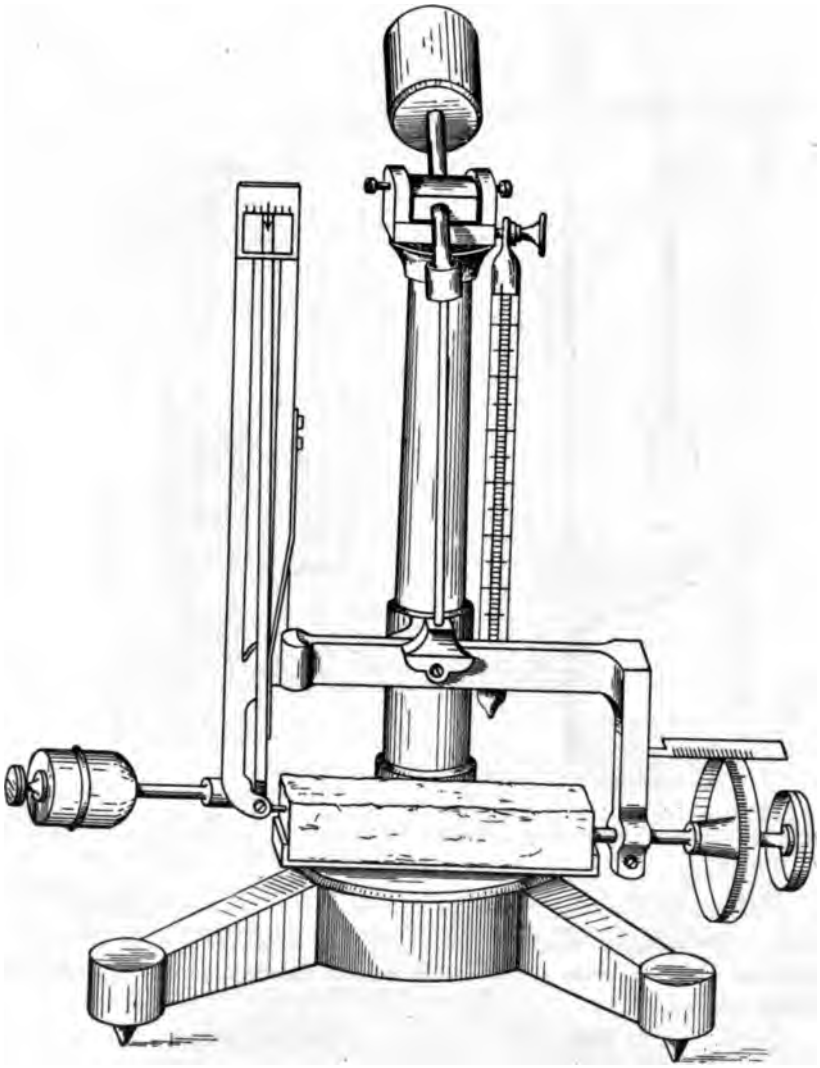

Fig. 71. Bauschinger apparatus for determining constancy of volume.

out by making a pat about 3 inches in diameter and 0.5 inch thick at the center, sloping to a thin edge on a clean glass plate. This pat of cement is then allowed to harden in an atmosphere of moist air for 24 hours. For the boiling test the specimen is put in cold water, which

is gradually heated till boiling and kept so for at least three hours. If the cement is sound the pat, though it may come off the glass plate, should be straight, free from radical cracks, and if a piece is broken off the edge it should break with a clear, sharp sound. If the pat is soft or cracked or partially disintegrated or warped, the cement is not considered sound.

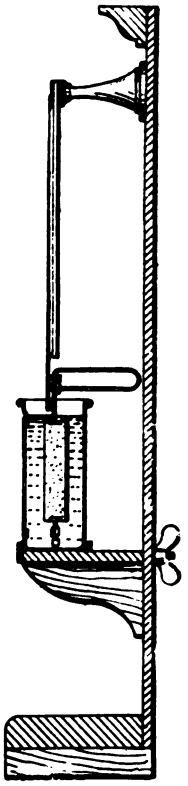

Fig. 72. Vertical section through Martens apparatus for measuring constancy of volume.

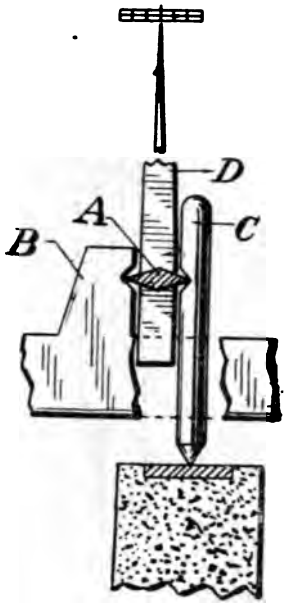

Fig. 73. Partial vertical cross-section through mechanism of Martens apparatus, showing method of transmitting and magnifying changes of length of cement block on which the apparatus rests.

The steam test differs only in that the pat is placed on a wire netting in an atmosphere of steam at about 90° C., without contact with water. This test is not as severe, as it eliminates the mechanical action of the boiling water.

In the warm water test the pat is placed in water at about 45° C. and kept there for 24 hours.

In the normal water test the pat simply remains in water at about 21° C. for 28 days. Any of the evidences mentioned under the boiling test will disqualify a cement. Warping may be detected by applying a straight edge to the surface which was in contact with the plate.

The boiling test is the most severe test and it may be said that, roughly speaking, nine out of ten cements which stand this test will be

found satisfactory in practice, but it is liable to reject cements which are really good. Thus a silicious cement may not pass this test simply because in the 24 hours its hardening has not progressed sufficiently to withstand the mechanical action of the water, while at the same time a rapidly hardened aluminous cement may test normally. In all these tests the mere coming off of the pat from the glass should not count against the cement.

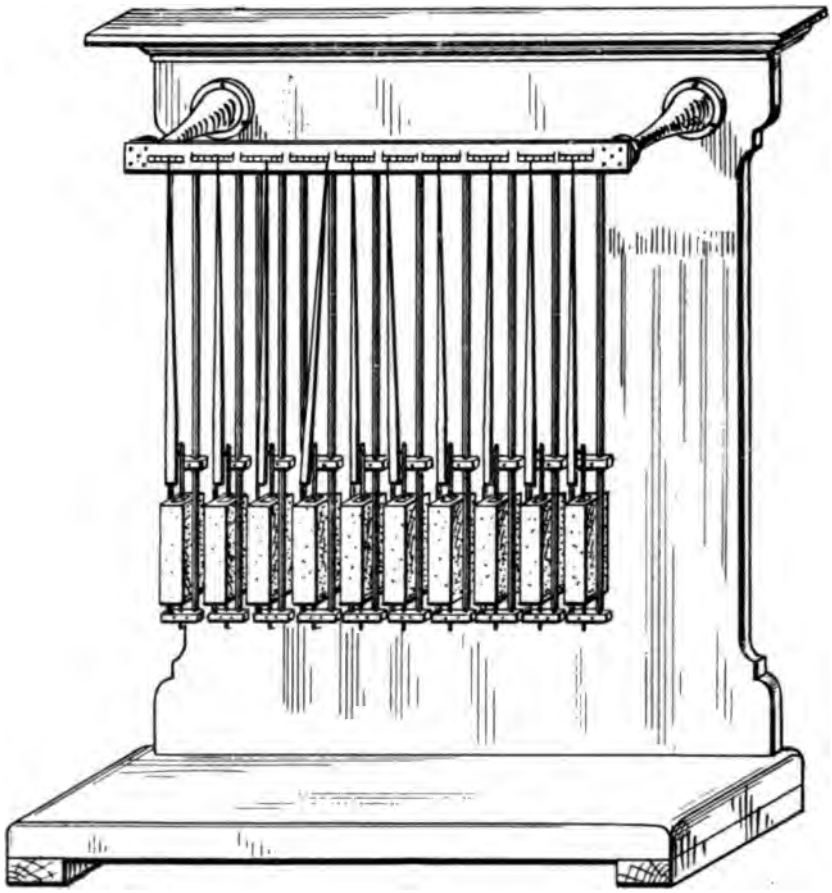

Fig. 74. A Martens apparatus, showing ten cement blocks under observation for change of volume.

The last word has not yet been said in regard to these tests and future work will clear up many difficulties attending our tests for constancy of volume.

In Europe still more rigid tests are practiced, like the hot flame test and the high pressure steam tests.

Calorimeter Test.—An auxiliary test made mention of before is the determination of the heat of hydration. It is well known that aluminous

cements like those containing excess of lime show a high heat of hydration, while the standard Portland cements, as well as cements with a high lime content, but a silicious clay base, have a low heat of hydration. As has been mentioned repeatedly, the number of calories given off on hydration by a cement are not intrinsically a sufficient criterion for judging the quality of a cement, but it is a fact that the standard American cements do not show a hydration value of over 8 calories per gram in excess of water. It has also been found that of cements made by the writer those which showed a high heat of hydration were apt to fail in the boiling test, though not always. The greatest help of this test is in estimating whether or not a cement has been stored sufficiently long. Many Portland cements would stand the hot test satisfactorily if they were allowed to cure longer, and the calorimeter test would thus tend to protect such fresh but otherwise good cements by indicating clearly that further storing is necessary.

The writer added to a sound Portland cement lime ignited to a high temperature in a crucible furnace in percentages varying from 1 to 6 per cent. Boiling tests showed no sign of the breaking down of the cements up to 4 per cent. On making calorimeter tests the heats of hydration determined practically form a straight line, as shown by the accompanying curve (figure 75). The abscissa indicates per cent. of caustic lime added, which was commercial lime, and the ordinate the calories per gram of cement mixture.

SPECIFIC GRAVITY.

The specific gravity of ignited Portland cement varies from 3.10 to 3.25. Storing invariably reduces the specific gravity. It has been frequently claimed that this constant furnishes a criterion in regard to whether the cement has been burnt properly or was underburnt. But extensive experiments have shown that this is not the case, since cement burnt just below vitrification has practically the same specific gravity as the properly burnt cement. It is of use, however, in estimating whether or not a given cement has been cured sufficiently and when this has been determined for a certain cement it affords the chemist a valuable aid in regulating the time of storing.

Overburnt cement shows a lower specific gravity than underburnt cement owing to the vesicular structure developed. It becomes evident, therefore, that the specific gravity does not deserve the general application it now receives except when it is applied to the detection of adulteration.

Specific Gravity Apparatus.—There are many instruments for the determination of specific gravity. The accompanying figure represents the apparatus designed by F. M. Meyer. The parts *a* and *b* are connected by means of a loose rubber tube. Through *h*, about 110 cm. of alcohol (redistilled over caustic lime) is poured in, lowering the bottle *f*. The marks *m*

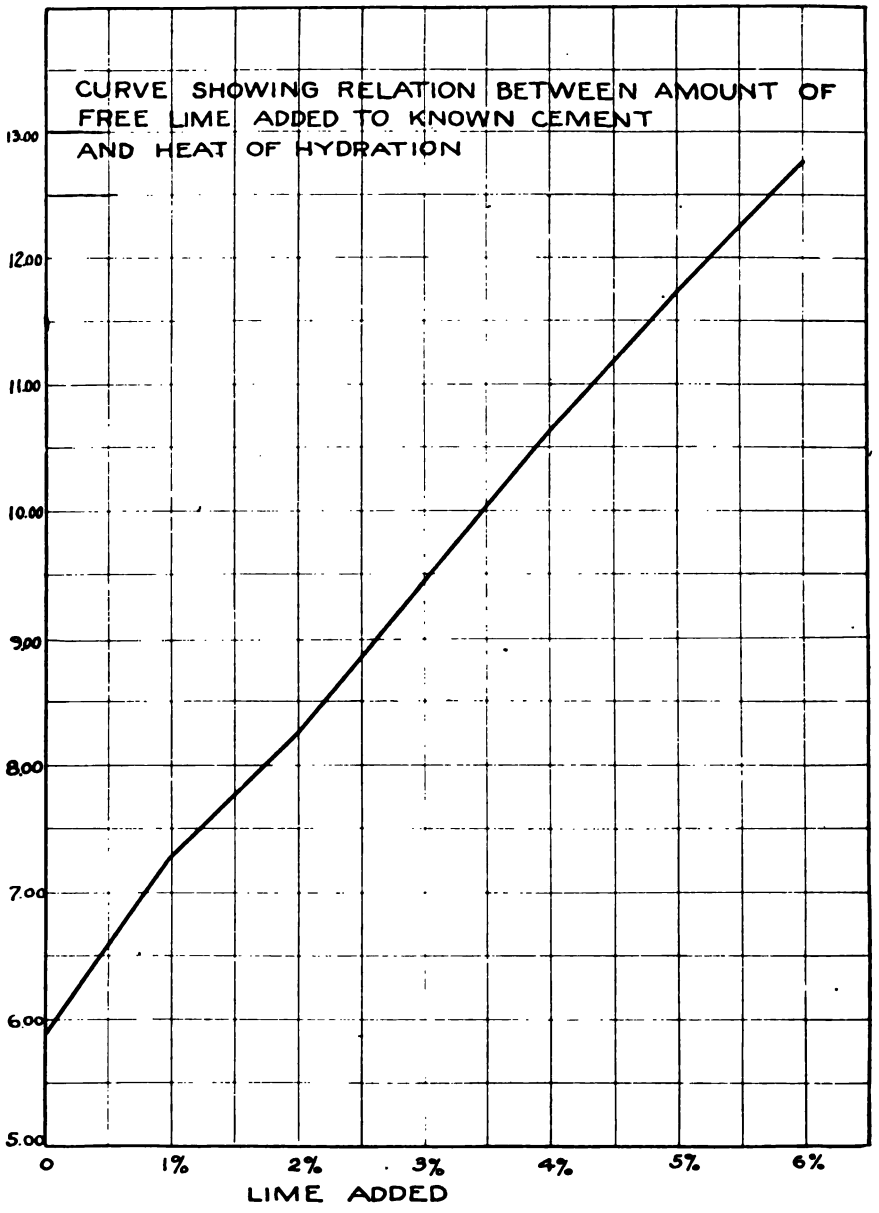

Fig. 75. Curves showing the regularity with which the calorimeter detects and measures the presence of free lime in Portland cement.

and m_1 are now brought to the same height and through the tube of the stopper s as much alcohol is poured as will bring the meniscus just below the marks m and m_1. By lifting the bottle f the burette is filled up to

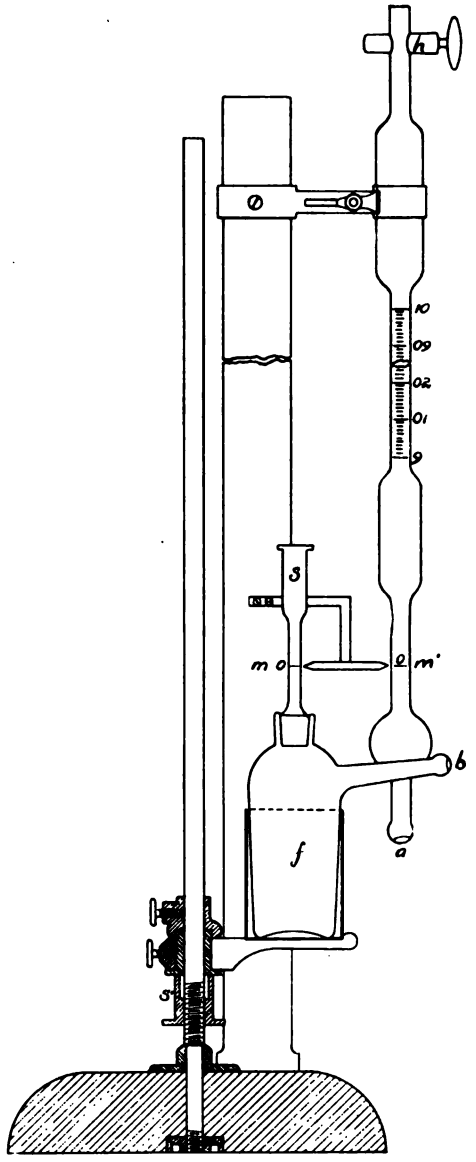

Fig. 71. The Meyer specific gravity apparatus.

the stopcock h, and f, without closing the cock, is brought to its original position. After 5 minutes, m and m_1 by pouring in more alcohol or by means of a micrometer screw are exactly defined. The outside of the stopper is then carefully dried with filter paper, f, raised till the alcohol

is close to the stopcock, *h*, and the latter closed. The stopper, *s*, is now removed and 30 grams of cement poured into the bottle, shaking it somewhat. The stopper is now replaced, *h* opened and *f* lowered till the alcohol reaches the mark *m*. After 3 minutes the volume of the cement can be read off the burette. From the volume and the weight of the cement the specific gravity is readily calculated from the formula

$$s=\frac{g}{v}$$

or it may be read off from a table. In this formula s represents the specific gravity, g the weight of the cement and v the volume displaced.

Liter Weight.—A constant of considerable significance, though not generally employed, is the weight of unit volume of cement, say one liter,

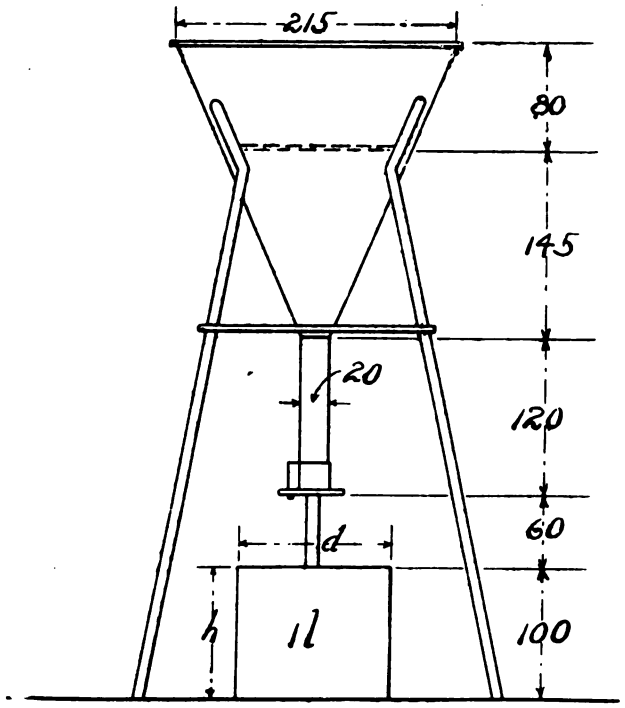

Fig. 77. Apparatus for determining weight of one liter of cement.

the cement being loose in the vessel employed for this purpose, not shaken. The liter weight is determined by placing a funnel over a copper vessel whose diameter is equal to its height and which contains exactly one liter. The lower part of the funnel is provided with a coarse sieve and the bottom of the funnel tube is 5 cm. above the edge of the vessel. Cement is now poured into the funnel in small quantities and when a cone is formed touching the funnel tube the excess of cement is scraped

off and the vessel, together with the cement, weighed. A sketch of the apparatus is shown in Figure 77.

FINENESS OF THE GRAIN.

All cement specifications include the point of fineness of grinding, as it is now generally recognized that the finer the cement is the more complete will be its hydration and the more sand will it be able to cement together. A number of well known investigations have brought this out so prominently that no further discussion is necessary.

The fineness of the cement is commonly measured by means of sieves, the 100 mesh screen being taken as the standard. Not more than 5 per cent. of the weight of the cement should be retained by the sieve, the wire being No. 40 of Stubbs' wire gauge. Finer sieves than the 150 mesh are not satisfactory for dry sieving, as they invariably tend to clog and give unreliable results. If they are to be used the cement should be put through wet, that is, made up into a thin paste with alcohol. In the nature of the case sieves cannot afford an accurate means of separating the really fine dust in a cement. This must be accomplished by means of the so-called mechanical analysis described at length in previous paragraphs.

Other means have also been suggested, like the separation by a current of air blown through a conical vessel, at a definite pressure, the current of air being conducted through a central pipe nearly to the bottom of the vessel. The fine particles are caught in a large cylinder. The air pressure is equal to a water column 3 inches high. The fine flour thus removed from commercial cements was found to be about 50 per cent. By increasing or reducing the pressure various sizes can be separated. An apparatus of this kind was proposed by W. F. Goreham.

SOME PHYSICAL AND CHEMICAL CONSTANTS.

The coefficient of expansion of pure Portland Cement is not of as great practical importance as that of the cement mortar or concrete. It is evident, of course, that the coefficient is somewhat influenced by the character of the aggregate in concrete. The coefficient of expansion of Portland cement, between 8° and 70° C. was found to be, by C. H. Au, 0.0000115 per degree C.

Bouniceau found the coefficient of expansion of concrete to be 0.0000137, that of wrought iron 0.00001235. This explains why reinforced concrete does not give rise to difficulties due to the differences in the coefficients of expansion, the expansion values of the concrete and iron being nearly the same. It might be mentioned here, also, that in reinforced concrete, according to the work of Considere, the tensile strength obtained approaches very closely that of the iron employed and cracking appears only when the tensile strains approach the elastic limit of the iron.

The specific heat of Portland cement clinker was found by Dr. Hart to be 0.19. The heat of hydration of a number of commercial Portland cements in excess of water was found to be not more than 8 calories per gram. In regard to the heat of solution of cements in acid, and other data, Meyer has worked out the following results. In this work he employed three cements of the following composition:

	Silica. Per cent.	Alumina. Per cent.	Ferric Oxide. Per cent.	Lime. Per. cent.	Magnesia. Per cent.
A.....	23.2	11.4	2.5	61.5	2.7
B.....	22.1	9.7	2.4	63.3	2.4
C.....	20.9	8.8	2.2	65.5	2.3

These cements were burnt at different temperatures and tested for specific gravity, alkalinity, constancy in volume and heat of solution.

Cement.	Burning temperature in Seger cones.	Specific gravity.	Alkalinity according to Fresenius.	Boiling test.	Heat of solution calories.	Expansion of 10 cm. prism, in per cent. In days.			
						3	7	28	90
A	12	3.243	6.6	friable	447	0.060	0.100	0.320	0.440
do	15	3.139	6.0	do	442	0.010	0.020	0.100	0.100
do	18	3.216	4.9	harder	447	0.025	0.050	0.120	0.180
do	21	3.159	5.6	hard	458	0.010	0.010	0.010	0.025
B	12	3.178	8.5	friable	470	0.010	0.025	0.065	0.125
do	15	3.199	6.5	hard	440	0.005	0.015	0.045	0.050
do	18	3.195	4.4	good	471	0.015	0.020	0.035	0.035
do	21	3.160	5.1	good	529	....	....	....	0.015
C	12	3.166	11.1	broke down	525	0.040	0.090	0.500	1.520
do	15	3.200	9.6	broke down	577	0.025	0.060	0.150	0.420
do	18	3.230	8.6	very friable	542	0.060	0.100	0.250	0.450
do	21	3.170	7.0	very friable	517	0.125	0.125	0.420	0.850

The "alkalinity" means the number of cc. of deci-normal acid used in neutralizing 50 cc. of distilled water which was in contact with 0.5 gram of cement.

Other physical and chemical constants determined by Dr. R. and Dr. W. Fresenius are given in the following table:*

Description.	1 Specific gravity.	2 Loss on ignition. Per cent.	3 Alkalinity imparted to water by 0.5 gram, cc. of decinormal acid.	4 Volume of normal acid neutralized by 1 gram.	5 Weight of K_2MnO_4, reduced by 1 gram.	Weight of (O), absorbed by 3 grams.
				cc.	mg.	mg.
Portland cement A	3.155	1.58	6.25	20.71	0.79	1.4
" " B	3.125	2.59	4.62	21.50	2.38	1.6
" " C	3.155	2.11	4.50	20.28	0.93	1.8
" " D	3.144	1.98	5.10	21.67	1.12	1.0
" " E	3.144	1.25	6.12	19.60	0.98	1.6
" " F	3.134	2.04	4.95	20.72	1.21	1.1
" " G	3.144	0.71	4.30	22.20	0.89	0.0
" " H	3.125	1.11	4.29	20.30	1.07	0.7
" " J	3.134	1.00	4.00	19.40	2.01	0.0
" " K	3.144	0.34	4.21	20.70	0.98	0.0
" " L	3.154	1.49	4.60	18.80	2.80	0.3
" " M	3.125	1.25	5.50	20.70	2.33	0.0

EFFECT OF VARIOUS REAGENTS ON PORTLAND CEMENT.

Since Portland cement is a very basic material, it is quite evident that it is readily attacked by acids and we find that even weak organic acids may exert a powerful solvent action upon this material. When mixed with sand, however, and especially if the resulting mortar is dense, the action is much less evident than on the neat cement. Even carbonic acid, carbon dioxide in solution in water, is able to act upon cement quite strikingly. On the other hand, salts show varying effects, as will be illustrated by a table. In common with colloids, hydrated cement has the property of taking salts from solution and of holding them by virtue of surface absorption, so that the concentration of such salts is greater in the colloid (hydrogel) than in the solution.

Gases like carbon dioxide, hydrogen sulphide, act upon cement quite energetically. Thus Tetmayer found that by storing four cements in air and in pure carbon dioxide the average tensile strength of

*R. K. Meade, *Examination of Portland Cement*, p. 167.

1:3 mortars was 29.4 kg. per square cm. for the cements stored in air and 45.3 kg. per square cm. for the cements exposed to pure carbon dioxide. The effect of moist air on cement is not as injurious as is often supposed. Sewage was found to have practically no effect upon standard cement mortar. Tar and mineral oils do not act upon cement; organic oils and the tannic acids form soaps with the lime of the cement which tend to soften the latter. This action, however, owing to surface incrustation, is of little importance in practical work. Of the materials added to cement for coloring purposes, like pyrolusite for black, iron or ochre for red and yellow, ultramarines for blue and green, only the latter do not decrease the ultimate strength. Ultramarine, in fact, has a strong tendency to increase the strength due to pozzuolanic action. Owing to the basic character of cements and the content of sulphates and alkalies, a number of minor reactions take place with the coloring constituents. Thus iron ore is in part attacked by the lime and bleached, as may be observed on the hollow blocks now used to so large an extent, the pyrolusite likewise is attacked and made, in part, soluble, while the ultramarine is decomposed in a comparatively short time, since its sulphur is removed by the lime of the cement. As the sulphides seem necessary for the color,on decomposition of the compound, $2(Na_2Al_2Si_3O_{10})+Na_2S_4$, the color must, of course, disappear. The addition of ground white marble does not help much in retaining these colors, but the grinding together of cement and white quartz, or white anhydrous silicates, would result in far greater permanency. Likewise the colors could be made permanent in themselves by being prepared as silicates. It seems to the writer that the Portland cement manufacturers should cater to this demand for prepared cement as well as to the production of white cements. The addition of such silicious matter would also tend to increase the durability of cement work in a most decided manner and would help remove the prejudice, justified in many cases, against architectural cement surfaces.

In the table on page 364, the effects of a number of salts upon the strength of Portland cement are shown:

It is true that many cements are apparently improved by the addition of gypsum in small amounts, but it has also been found that high grade cements show practically no improvement. Dr. Erdmenger's work proves quite strikingly that the gypsum is a source of weakness which should be kept within the lowest possible limit.

THE ENDURING QUALITIES OF PORTLAND CEMENT.

As has already been indicated, Portland cement, like all basic hydrous rocks, is subject to rather rapid destruction by atmospheric agencies if exposed without the addition of sand. It has also been found that

Erdmenger's Table Showing Effect of Various Salts on the Behavior of Portland Cements.

Substance added.	Time of setting minutes.			Tensile strength neat, 28 days, kg. per sq. cm.			Tensile strength 1:3, 28 days, kg. per sq. cm.		
Cement alone ..	10 minutes.			40.8			13.3		
Per cent added.	1%	2%	5%	1%	2%	5%	1%	2%	5%
Raw gypsum...	240	360	360	56.5	62.6	26.4	19.9	....	....
Potass. sulphate	4	2	5	41.3	35.2	34.2	16.7	13.8	....
Sodium sulph'te	15	5	5	43.2	46.0	43.2	19.4	19.0	....
Ammon sulph..	120	300	480	54.4	35.3	....	15.1	....	....
Magnes. sulph.	15	480	24 hrs.	48.1	37.1	46.3	15.5	14.3	....
Alumin. sulph.	15	10	30	40.0	40.0	34.3	16.4	16.7	....
Iron sulphate..	360	720	240	48.0	41.9	34.5	15.9	....	....
Alum.....	10	30	40	41.7	40.7	....	14.9	....	....
Caustic potash.	....	3	.....	....	29.4	....	....	15.1	....
Ammonium.... hydroxide....	....	3	.....	....	46.8	....	....	17.5	....

some Portland cement mortars were destroyed at an alarming rate in sea water, and consequently a vast mass of literature exists on this point and the data collected are exceedingly contradictory and confusing. However, thanks to the work of the German Portland Cement Manufacturers' Association, some light has been thrown on the action of sea water, and though the experiments carried on by this society on a large scale are not yet finished, it is known now that there is little danger for sea water work if the mortar is made dense and good Portland cement is used.

The supposed destruction of Portland cement concrete is said to be due to the magnesium content of sea water and formation of calcium-aluminum sulphates. The alumina is said to be especially injurious and gypsum also is a source of danger in this respect. Rebuffat ascribes the partial solution of the cement to the formation of sulfo-aluminates. Michaelis and Vicat think that the action is based on the reaction:

$$Ca(OH)_2+MgSO_4=Mg(OH)_2+CaSO_4$$

which, owing to the formation of crystalline calcium sulphate, causes an

increase in volume and thus destroys the mortar. A number of other investigators have attacked the problem like Chatelier, Debray, Feret, Deval and others. The results may be summarized by saying that the alumina and gypsum are the weak points of the cement while the ferric oxide is beneficial. The cements should be as silicious and as high in ferric oxide as possible.

Addition of Pozzuolane.—Michaelis, Sr., has also shown that the resistance of Portland cement to sea water may be increased enormously by the addition of pozzuolanic material, like trass. If trass or a similar material is not available, there is no reason whatever why well burnt clay may not be used; in fact, the writer has found that just as natural cements are improved by the addition of slaked lime,the reaction may be reversed in the case of the basic Portland cements by adding pozzuolanic material or ground burnt clay. Thus we increase the resulting strength by the addition of a secondary hydraulic reaction and obtain as the resulting strength the initial strength of the Portland cement plus the strength derived from the secondary, pozzuolanic action. In addition, by virtue of the secondary reaction, the resistance of the cement to all kinds of influence is increased by the more silicious character of the mortar. This idea has been carried out in the production of the so-called sand cement, which is simply ordinary Portland cement ground together with trass or sand, and is sold for sea water work. The writer has seen such a plant at Staten Island and another one is reported to be at Chicago. In one of these plants, however, the chemical principle underlying their process was not understood, for in place of the sand, limestone was used because it was easier to grind. This evidently could not improve the cement in the desired direction, though an increase in tensile strength might be observed, independent of any pozzuolanic action, due simply to the second grinding of the cement.

It would be interesting to observe cement work in which the cement was ground together with well burnt clay under adverse conditions, that is, exposed to water containing carbonic acid or any water of acid reaction. Experiments conducted by the writer on a small scale in which cement was ground together in a ball-mill with burnt clay in the proportion of 1:1 showed a much greater resistance to the action of acidulated water (hydrochloric) than cement mortar not so treated. But the laboratory results of such experiments are, as a rule, not comparable with the practical results. If, however, practice should confirm this suggestion, the durability of exposed cement surfaces, of reservoir walls, sea walls, piers, cement blocks would thus be improved cheaply and satisfactorily. It should be the task of Portland cement manufacturers to study these questions and to prepare for the market cements especially suitable for exposed work. Much of the lack of confidence which has existed in certain quarters in years past in the use of cement would thus be eliminated.

Efflorescence.—A great source of annoyance is frequently the appearance of soluble salts on the surface of cement work, giving rise to disagreeable patches of so-called "whitewash." These salts are principally sulphates of the alkalies, lime, magnesia and iron, and can to a large extent be prevented by the addition of fine barium carbonate to the mortar, which takes up the available sulphuric acid and forms the insoluble barium sulphate according to the reaction:

$$CaSO_4+BaCO_3=CaCO_3+BaSO_4.$$

Excess of the barium carbonate should be used. The barium chloride is more efficient, a smaller amount being sufficient owing to its solubility in water, but any excess will in itself produce a white efflorescence. For decorative purposes cement with a silicious clay base free from gypsum should be used.

Another method of preventing efflorescence is the application of a solution of silicon fluoride of magnesium or lead. This solution reacts with the lime of the cement forming an insoluble double silicon fluoride.

Dr. Michaelis* advocates the use of a dilute water glass solution which is applied several times and finally the surface is washed thoroughly with water to remove the alkalies which have become free by the combination of the silicic acid with the lime.

For preparing a cement surface for painting Dr. Fruehling** recommends an ammonium carbonate solution applied upon the hardened cement.

Adulteration.—Sometimes it is found that Portland cement is adulterated with ground slag and it becomes necessary to detect the presence of the latter, or again natural cement may be the adulterant. Such constituents may be detected by means of the following differentiation:

1. Portland cement has a higher specific gravity than either the natural cement or slag.

2. The loss on ignition of natural cement is much greater than that of Portland cement.

3. The amount of carbon dioxide absorbed by natural cement may be greater than that taken up by Portland cement.

4. Owing to the high content of sulphides in slag the amount of potassium permanganate decolorized by slag is much greater than that consumed by Portland cement, and of course the amount of sulphide sulphur is much larger in amount.

Mechanical Separation.—The difference in specific gravity is employed to separate the admixed substances from the Portland cement. This is carried out as follows: By means of the 20, 30 and 40 mesh

*Dr. Michaelis, *Die Hydraulischen Moertel*, 313.
**Polytech, *Centralblatt*, 1871, p. 261.

sieves two sizes of grain, a and b, are separated and carefully dried. Of each size 5 grams are taken and shaken in a dry Haradas separatory funnel with a mixture of methyl iodide and purified oil of turpentine. This mixture should have at 15° C. a specific gravity of 3.01. The methyl iodide before being used should be dried over calcium chloride and filtered through previously ignited Portland cement. A hydrometer may be used for determining the specific gravity of the liquid. A suction pump is now attached to the funnel and the particles are separated according to whether they are lighter or heavier than 3.01.

The light particles which float are:

1. Coal, mean specific gravity, 1.39.
2. Gypsum, mean specific gravity, 2.33.
3. Coal cinders, mean specific gravity, 2.73.
4. Natural cement, mean specific gravity, 2.60.
5. Blast furnace slag, mean specific gravity, 2.94.

The heavier particles which sink are:

1. Portland cement, mean specific gravity, 3.10.
2. Particles of slag, high in iron, or particles of metallic iron.

In unadulterated Portland cement the amount of light material is small and hence any large amount of matter floating in the liquid is to be regarded as suspicious. Chemical analysis, including the determination of sulphide sulphur, will show whether the light material is natural cement or slag. In both cases the separated particles will analyze much lower in lime than the Portland cement. The presence of sulphide will indicate that the inert matter is slag.

In the following table some of the characteristics of natural cement and slag are indicated:*

Description.	Specific gravity.	Loss on ignition. Per cent.	Alkalinity imparted to water by 0.5 gram. cc. of decinormal acid.	Volume of normal acid neutralized by 1 gram. In c.c.	Weight of potassium permang. reduced by 1 gram. In mg's.	Weight of carbon dioxide absorbed by 3 grams. In mg's.
Hydraulic lime A..	2.441	18.26	20.23	21.35	1.40	27.8
" " B..	2.551	17.82	22.73	26.80	0.93	31.3
" " C..	2.520	19.60	19.72	19.96	0.98	47.7
Weathered slag A..	3.012	0.76	0.91	14.19	74.60	3.6
" " B..	3.003	1.92	0.70	13.67	60.67	3.5
" " C..	2.967	1.11	1.00	9.70	44.34	2.9
Ground slag D..	3.003	0.32	0.31	3.60	64.40	2.4
" " E..	2.873	0.43	0.11	8.20	73.27	2.2

*Meade, *Examination of Portland Cement.*

CEMENT SPECIFICATIONS.

In the following paragraphs the rules proposed by a committee of the American Society of Civil Engineers for the testing of Portland cement are given which were submitted to the society, January, 1903:

On several matters which have been considered, such as the substitution of a natural sand for the standard quartz, and the tests for the normal consistency and constancy of volume, the committee has not reached final conclusions.

SAMPLING.

1. Selection of Sample.—The selection of the sample for testing is a detail that must be left to the discretion of the engineer; the number and the quantity to be taken from each package will depend largely on the importance of the work, the number of tests to be made and the facilities for making them.

2. The sample shall be a fair average of the contents of the package; it is recommended that, where conditions permit, one barrel in every ten be sampled.

3. All samples should be passed through a sieve having twenty meshes per linear inch, in order to break up lumps and remove foreign material; this is also a very effective method for mixing them together in order to obtain an average. For determining the characteristics of a shipment of cement, the individual samples may be mixed and the average tested; where time will permit, however, it is recommended that they be tested separately.

4. Method of Sampling.—Cement in barrels should be sampled through a hole made in the center of one of the staves, midway between the heads, or in the head, by means of an auger or a sampling iron similar to that used by sugar inspectors. If in bags, it should be taken from surface to center.

CHEMICAL ANALYSIS.

5. Significance.—Chemical analysis may render valuable service in the detection of adulteration of cement with considerable amount of inert material, such as slag or ground limestone. It is of use, also, in determining whether certain constituents, believed to be harmful when in excess of a certain percentage, as magnesia and sulphuric anhydride, are present in inadmissible proportions. While not recommending a definite limit for these impurities, the committee would suggest that the most recent and reliable evidence appears to indicate that magnesia to the amount of 5 per cent. and sulphuric anhydride to the amount of 1.75 per cent. may safely be considered harmless.

6. The determination of the principal constituents of cement, silica, alumina, iron oxide and lime is not conclusive as an indication of quality. Faulty character of cement results more frequently from imperfect preparation of the raw material or defective burning than from incorrect pro-

portions of the constituents. Cement made from very finely-ground material, and thoroughly burned, may contain much more lime than the amount usually present and still be perfectly sound. On the other hand, cement low in lime may, on account of careless preparation of the raw material, be of dangerous character. Further, the ash of the fuel used in burning may so greatly modify the composition of the product as largely to destroy the significance of the results of analysis.

7. **Method.**—As a method to be followed for the analysis of cement, that proposed by the committee on uniformity in the analysis of materials for the Portland cement industry, of the New York section of the Society for Chemical Industry, and published in the Journal of the Society for January 15, 1902, is recommended.

SPECIFIC GRAVITY.

8. **Significance.**—The specific gravity of cement is lowered by underburning, adulteration and hydration, but the adulteration must be in considerable quantity to affect the results appreciably.

9. Inasmuch as the differences in specific gravity are usually very small, great care must be exercised in making the determination.

10. When properly made, this test affords a quick check for underburning or adulteration.

11. **Apparatus and Method.**—The determination of specific gravity is most conveniently made with Le Chatelier's apparatus. This consists of a flask (D) (figure 78) of 120 cu.cm. (72.32 cu. in.) capacity, the neck of which is about 2 cm. (7.87 in.) long; in the middle of the neck is a bulb (C), above and below which are two marks (F) and (E); the volume between these marks is 20 cu. cm. (1.22 cu. in.). The neck has a diameter of about 9 mm. (0.35 in.), and is graduated into tenths of cubic centimeters above the bulb.

12. Benzine (62° Baume) naptha, or kerosene free from water, should be used in making the determination.

13. The specific gravity can be determined in two ways:

(1.) The flask is filled with either of these liquids to the lower mark (E), and 64 gr. (2.25 oz.) of powder, previously dried at 100° C. (212° F.) and cooled to the temperature of this liquid, is gradually introduced through the funnel (B) the stem of which extends into the flask to the top of the bulb (C)), until the upper mark (F) is reached. The difference in weight between the cement remaining and the original quantity (64 gr.) is the weight which has displaced 20 cu. cm.

14. (2) The whole quantity of the powder is introduced, and the level of the liquid rises to some division of the graduated neck. This reading plus 20 cu. cm. is the volume displaced by 64 gr. of the powder.

15. The specific gravity is then obtained from the formula:

$$\text{Specific Gravity} = \frac{\text{Weight of Cement}}{\text{Displaced Volume}}$$

16. The flask, during the operation, is kept immersed in water in a jar (A), in order to avoid variations in the temperature of the liquid. Duplicate results should agree to 0.01.

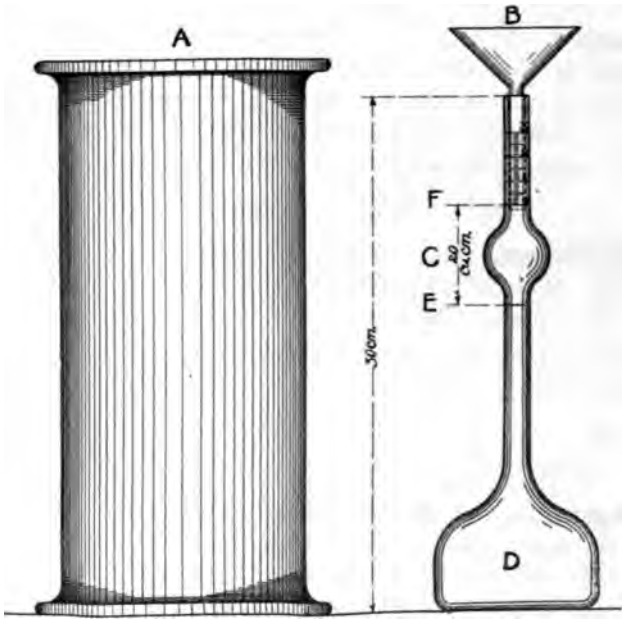

Fig. 73. Specific gravity apparatus, according to Le Chatelier.

17. A convenient method for cleaning the apparatus is as follows: The flask is inverted over a large vessel, preferably a glass jar, and shaken vertically until the liquid starts to flow freely; it is then held still in a vertical position until empty; the remaining traces of cement can be removed in a similar manner by pouring into the flask a small quantity of clean liquid and repeating the operation.

18. More accurate determinations may be made with the pincometer.

FINENESS.

19. Significance.—It is generally accepted that the coarser particles in cement are practically inert, and it is only the extremely fine powder that possesses adhesive or cementing qualities. The more finely cement is pulverized, all other conditions being the same, the more sand it will carry and produce a mortar of a given strength.

20. The degree of final pulverization which the cement received at the place of manufacture is ascertained by measuring the residue retained

on certain sieves. Those known as the No. 100 and No. 200 sieves are recommended for this purpose.

21. **Apparatus.**—The sieves should be circular, about 20 cm. (7.87 in.) in diameter, 6 cm. (2.36 in.) high, and provided with a pan, 5 cm. (1.97 in.) deep, and a cover.

22. The wire cloth should be woven (not twilled) from brass wire having the following diameters:

No. 100, 0.0045 in.; No. 200, 0.0024 in.

23. This cloth should be mounted on the frames without distortion; the mesh should be regular in spacing and be within the following limits:

No. 100, 96 to 100 meshes to the linear inch.

No. 200, 188 to 200 meshes to the linear inch.

24. Fifty grams (1.76 oz.) or 100 gr. (3.52 oz.) should be used for the test and dried at a temperature of 100° C. (212° F.) prior to sieving.

25. **Method.**—The committee, after careful investigation, has reached the conclusion that mechanical sieving is not as practicable or efficient as hand work, and, therefore, recommends the following method:

26. The thoroughly dried and coarsely screened sample is weighed and placed on the No. 200 sieve, which, with pan and cover attached, is held in one hand in a slightly inclined position, and moved forward and backward, at the same time striking the side gently with the palm of the other hand, at the rate of about 200 strokes per minute. The operation is continued until not more than one-tenth of one per cent. passes through after one minute of continuous sieving. The residue is weighed, then placed on the No. 100 sieve and the operation repeated. The work may be expedited by placing in the sieve a small quantity of large shot. The results should be reported to the nearest tenth of 1 per cent.

NORMAL CONSISTENCY.

27. **Significance.**—The use of a proper percentage of water in making the pastes* from which pats, tests of setting and briquettes are made, is exceedingly important, and affects vitally the results obtained.

28. The determination consists in measuring the amount of water required to reduce the cement to a given state of plasticity, or to what is usually designated normal consistency.

29. Various methods have been proposed for making this determination, none of which have been found entirely satisfactory. The committee recommends the following:

30. **Method. Vicat Needle Apparatus.**—This consists of a frame (K), (Figure 79) bearing a movable rod (L), with the cap (A) at one

*The term "paste" is used in this report to designate a mixture of cement and water, and the word "mortar" a mixture of cement, sand and water.

end, and at the other end the cylinder (B), 1 cm. (0.39 in.) in diameter, the cap, rod and cylinder weighing 300 gr. (10.58 oz.). The rod, which can be held in any desired position by a screw (F) carries an indicator,

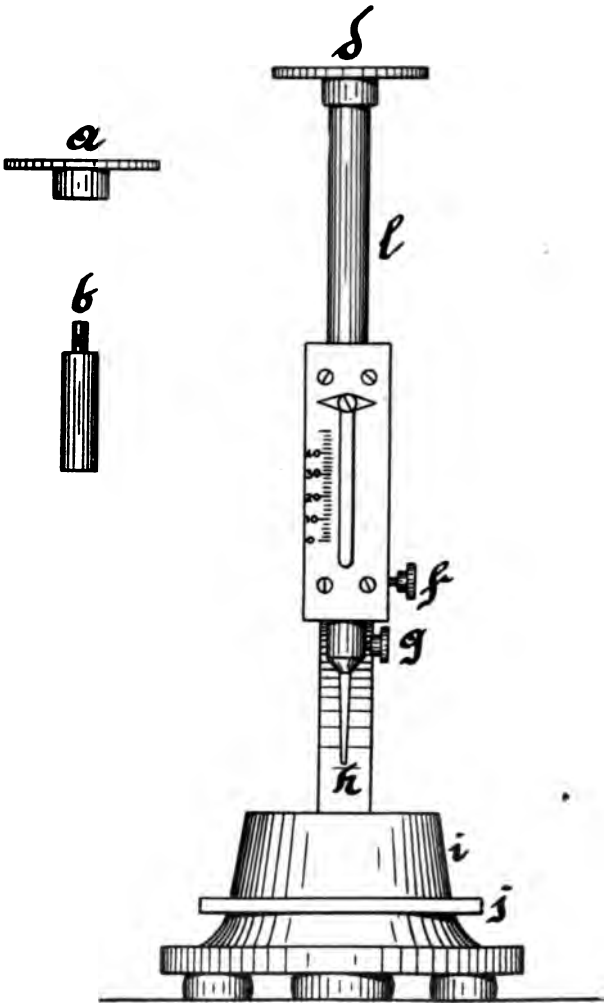

Fig. 79. Vicat's needle for measuring standard consistency of cement mortars, and also detecting moment of initial hardening.

which moves over a scale (graduated to millimeters) attached to the frame (K). The paste is held by a conical, hard-rubber ring (I), 7 cm. (2.76 in.) in diameter at the base, 4 cm. (1.57 in.) high, resting on a glass plate (J), about 10 cm. (3.94 in.) square.

31. In making the determination, 500 gr. (17.64 oz.) of cement are kneaded into a paste, as described in paragraph 58, and quickly formed into a ball with the hands, completing the operation by tossing

it six times from one hand to the other, maintained 6 inches apart; the ball is then pressed into the rubber ring, through the larger opening, smoothed off, and placed on a glass plate (on its large end) and the smaller end smoothed off with a trowel; the paste, confined in the ring, resting on the plate, is placed under the rod bearing the cylinder, which is brought in contact with the surface and quickly released.

32. The paste is of normal consistency when the cylinder penetrates to a point in the mass 10 mm. (0.39 in.) below the top of the ring Great care must be taken to fill the ring exactly to the top.

33. The trial pastes are made with varying percentages of water until the correct consistency is obtained.

34. The committee believes that the normal consistency should produce a rather wet paste, since this consistency tends to greater uniformity in the mixing, and there is less liability of compressing the briquettes during the molding.

35. Having determined in this manner the proper percentage of water required to produce a neat paste of normal consistency, the proper percentage required for the sand mortars is obtained from an empirical formula.

36. The committee hopes to devise such a formula. The subject proves to be a very difficult one, and, although the committee has given it much study, it is not yet prepared to make a definite recommendation.

TIME OF SETTING.

37. Significance.—The object of this test is to determine the time which elapses from the moment water is added until the paste ceases to be fluid and plastic (called the "initial set"), and also the time required for it to acquire a certain degree of hardness (called the "final" or "hard set"). The former of these is the more important, since, with the commencement of setting, the process of crystallization or hardening is said to begin. As a disturbance of this process may produce a loss of strength, it is desirable to complete the operation of mixing and molding or incorporating the mortar into the work before the cement begins to set.

38. It is usual to measure arbitrarily the beginning and end of the setting by the penetration of weighted wires of given diameters.

39. Method.—For this purpose the Vicat needle, which has already been described in paragraph 30, should be used.

40. In making the test, a paste of normal consistency is molded and placed under the rod (L) (figure 79), as described in paragraph 31; this rod, bearing the cap (D) at one end and the needle (H), 1 mm. (0.039 in.) in diameter at the other, weighing 300 gr. (10.58 oz.). The needle is then carefully brought in contact with the surface of the paste and quickly released.

41. The setting is said to have commenced when the needle ceases to pass a point 5 mm. (0.20 in.) above the upper surface of the glass plate, and is said to have terminated the moment the needle does not sink visibly into the mass.

42. The test pieces should be stored in moist air during the test; this is accomplished by placing them on a rack over water contained in a pan and covered with a damp cloth, the cloth to be kept away from them by means of a wire screen; or they may be stored in a moist box or closet.

43. Care should be taken to keep the needle clean, as the collection of cement on the sides of the needle retards the penetration, while cement on the point reduces the area and tends to increase the penetration.

44. The determination of the time of setting is only approximate, being materially affected by the temperature of the mixing water, the temperature and humidity of the air during the test, the percentage of water used, and the amount of molding the paste receives.

STANDARD SAND.

45. The committee recognizes the grave objections to the standard quartz now generally used, especially on account of its high percentage of voids, the difficulty of compacting in the molds, and its lack of uniformity; it has spent much time in investigating the various natural sands which appeared to be available and suitable for use.

46. For the present the committee recommends the natural sand from Ottawa, Ill., screened to pass a sieve having 20 meshes per linear inch and retained on a sieve having 30 meshes per linear inch; the wires to have diameters of 0.0165 and 0.0112 inch, respectively, i. e., half the width of the opening in each case.

47. The Sandusky Portland Cement Company, of Sandusky, Ohio, has agreed to undertake the preparation of this sand, and to furnish it at a price only sufficient to cover the actual cost of preparation.

FORM OF BRIQUETTE.

48. While the form of a briquette recommended by a former committee of the society is not wholly satisfactory, this committee is not prepared to suggest any change, other than rounding off the corners by curves of 1½ inch radius (figure 80).

MOLDS.

49. The molds should be made of brass, bronze or some equally non-corrodible material, having sufficient metal in the sides to prevent spreading during molding.

50. Gang molds, which permit molding a number of briquettes at one time, are preferred by many to single molds, since the greater quantity

of mortar that can be mixed tends to produce greater uniformity in the results.

51. The molds should be wiped with an oily cloth before using.

52. All proportions should be stated by weight; the quantity of water to be used should be stated as a percentage of the dry material.

53. The metric system is recommended because of the convenient relation of the gram and the cubic centimeter.

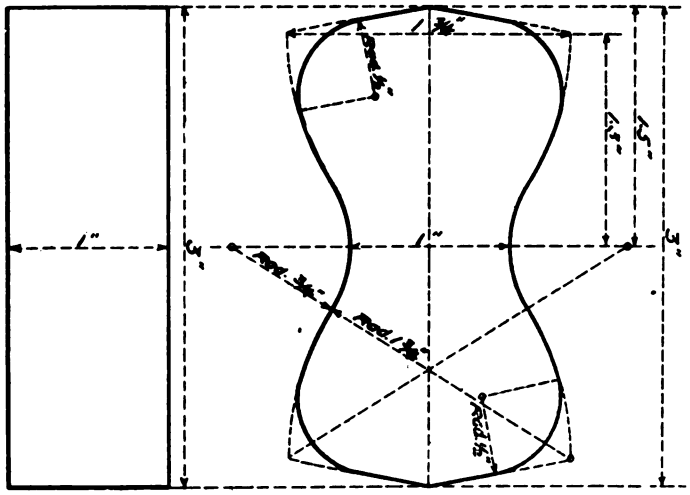

Fig. 80. Standard form of brickette for tensile strength.

54. The temperature of the room and the mixing water should be as near 21° C. (70° F.) as it is practicable to maintain it.

55. The sand and cement should be thoroughly mixed dry. The mixing should be done on some non-absorbing surface, preferably plate glass. If the mixing must be done on an absorbing surface it should be thoroughly dampened prior to use.

56. The quantity of material to be mixed at one time depends on the number of test pieces to be made; about 1,000 gr. (35.28 oz.) makes a convenient quantity to mix, especially by hand methods.

57. The committee, after investigation of the various mechanical mixing machines, has decided not to recommend any machine that has thus far been devised, for the following reasons: (1) The tendency of most cement is to "ball up" in the machine, thereby preventing the working of it into a homogeneous paste; (2) There are no means of ascertaining when the mixing is complete without stopping the machine, and (3) the difficulty of keeping the machine clean.

58. **Method.**—The material is weighed and placed on the mixing table, and a crater formed in the center, into which the proper percentage

of water is poured; the material on the outer edge is turned into the crater by the aid of a trowel. As soon as the water has been absorbed, which should not require more than one minute, the operation is completed by vigorously kneading with the hands for an additional 1½ minutes, the process being similar to that used in kneading dough. A sand-glass affords a convenient guide for the time of kneading. During the operation of mixing, the hands should be protected by gloves, preferably of rubber.

MOLDING.

59. Having worked the paste or mortar to the proper consistency, it is at once placed in the molds by hand.

60. The committee has been unable to secure satisfactory results with the present molding machines; the operation of machine molding is very slow, and the present types permit of molding but one briquette at a time, and are not practicable with the pastes or mortars herein recommended.

61. Method.—The molds should be filled at once, the materials pressed in firmly with the fingers and smoothed off with a trowel without ramming; the material should be heaped up on the upper surface of the mold, and, in smoothing off, the trowel should be drawn over the mold in such a manner as to exert a moderate pressure on the excess material. The mold should be turned over and the operation repeated.

62. A check upon the uniformity of the mixing and molding is afforded by weighing the briquettes just prior to immersion, or upon removal from the moist closet. Briquettes which vary in weight more than 3 per cent. from the average should not be tested.

STORAGE OF THE TEST PIECES.

63. During the first 24 hours after molding, the test pieces should be kept in moist air to prevent them from drying out.

64. A moist closet or chamber is so easily devised that the use of of the damp cloth should be abandoned if possible. Covering the test pieces with damp cloth is objectionable, as commonly used, because the cloth may dry out unequally, and, in consequence, all the test pieces are not maintained under the same condition. Where a moist closet is not available, a cloth may be used and kept uniformly wet by immersing the ends in water. It should be kept from direct contact with the test pieces by means of a wire screen or some similar arrangement.

65. The moist closet consists of a soapstone or slate box, or a metal-lined wooden box—the metal lining being covered with felt and this felt kept wet. The bottom of the box is so constructed as to hold water, and the sides are provided with cleats for holding glass shelves on which to place the briquettes. Care should be taken to keep the air in the closet uniformly moist.

66. After 24 hours in moist air, the test pieces for longer periods of time should be immersed in water maintained as near 21° C. (70° F.) as practicable; they may be stored in tanks or pans, which should be of non-corrodable materials.

TENSILE STRENGTH.

67. The tests may be made on any standard machine. A solid metal clip, as shown in figure 81, is recommended. The clip is to be used without cushioning at the points of contact with the test specimen. The bearing at each point of contact should be ¼ inch wide, and the distance between the center of contact on the same slip should be 1¼ inches.

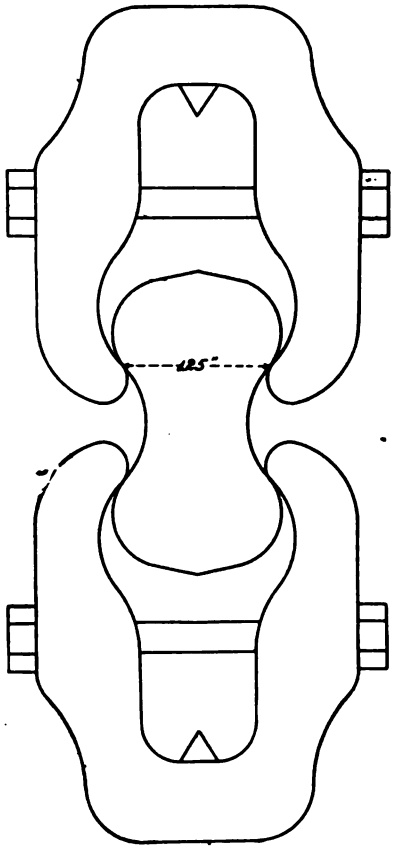

Fig. 81. Standard form of clips for holding tensile test pieces.

68. Test pieces should be broken as soon as they are removed from the water. Care should be observed in centering the briquettes in the testing machine, as cross-strains produced by improper centering tend to lower the breaking strength. The load should not be applied too suddenly, as it may produce vibration, the shock from which often

breaks the briquette before the ultimate strength is reached. Care must be taken that the clips and the sides of the briquettes be clean and free from sand or dirt, which would prevent a good bearing. The load should be applied at the rate of 600 pounds per minute. The average of the briquettes of each sample tested should be taken as the test, excluding any results which are manifestly faulty.

CONSTANCY OF VOLUME.

69. Significance.—The object is to develop those qualities which tend to destroy the strength and durability of a cement. As it is highly essential to determine such qualities at once, tests of this character are for the most part made in a very short time, and are known, therefore, as accelerated tests. Failure is revealed by cracking, checking, swelling or disintegration, or all of these phenomena. A cement which remains perfectly sound is said to be of constant volume.

70. Method.—Tests for constancy of volume are divided into two classes: (1) normal tests, or those made in either air or water maintained at about 21° C. (70° F.) and (2) accelerated tests, or those made in air, steam or water at a temperature of 45° C. (115° F.) and upwards. The test pieces should be allowed to remain 24 hours in moist air before immersion in water or steam.

71. For these tests, pats, about 7½ cm. (2.95 in.) in diameter, 1¼ cm. (0.49 in.) thick at the center, and tapering to a thin edge, should be made, upon a clean glass plate (about 10 cm. (3.94 in.) square), from cement paste of normal consistency.

72. Normal Test.—A pat is immersed in water maintained as near 21° C. (70° F.) as possible for 28 days and observed at intervals; the pat should remain firm and hard and show no signs of cracking, distortion or disintegration.

73. Accelerated Test.—(a) A pat is placed on a shelf in a suitable vessel filled with fresh water, but without allowing it to touch the bottom. The water is then gradually raised to a temperature of 45° C. (115° F.) and maintained at this temperature for 24 hours; or (b), a pat is exposed in any convenient way in an atmosphere of steam, above boiling water, in a loosely closed vessel, for 3 hours.

74. To pass these tests satisfactorily, the pats should remain firm and hard, and show no signs of cracking, distortion or disintegration.

75. Should the pat leave the plate, distortion may be detected best with a straight-edge applied to the surface which was in contact with the plate.

76. In the present state of our knowledge it cannot be said that cement should necessarily be condemned simply for failure to pass the accelerated tests; nor can a cement be considered entirely satisfactory simply because it has passed these tests.

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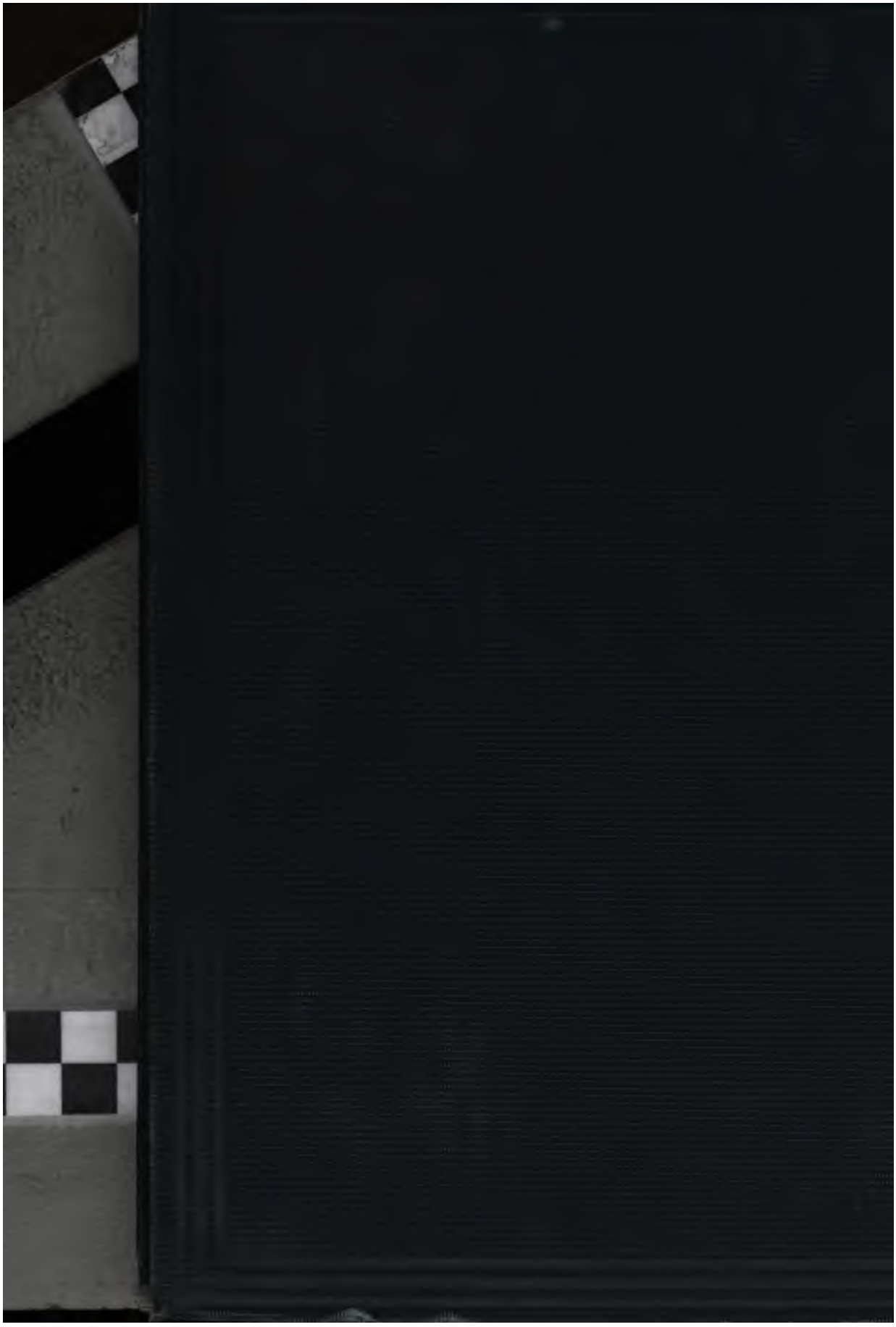
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